

From the simple reacting sphere kinetic model to the reaction-diffusion system of Maxwell-Stefan type

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Abstract

In this paper we perform a formal asymptotic analysis on a kinetic model for reactive mixtures in order to derive a reaction-diffusion system of Maxwell-Stefan type. More specifically, we start from the kinetic model of simple reacting spheres for a quaternary mixture of monatomic ideal gases that undergoes a reversible chemical reaction of bimolecular type. Then, we consider a scaling describing a physical situation in which mechanical collisions play a dominant role in the evolution process, while chemical reactions are slow, and compute explicitly the production terms associated to the concentration and momentum balance equations for each species in the reactive mixture. Finally, we prove that, under the isothermal assumption, the limit equations for the scaled kinetic model is the reaction diffusion system of Maxwell-Stefan type.

Keywords: Boltzmann-type equations. Chemically reactive mixtures. Diffusion limit. Kinetic theory of gases. Maxwell-Stefan equations.

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1 Introduction

The description and modelling of chemically reactive mixtures is a topic of great importance due to many engineering applications related, for example, to chemical industry and biotechnology [17, 35, 39]. In particular, a proper description of diffusive phenomena in multicomponent mixtures, with or without chemical reactions, is crucial in many simulations and design processes used by chemical engineers [27]. In this context, the Maxwell-Stefan (MS) equations are used by many applied and experimental researchers to model and predict diffusion as well as mass transfer processes in multicomponent mixtures [35, 36, 39]. In fact, it is well known that the MS equations are adequate to describe non-typical diffusions that appear as a consequence of some thermodynamic non-idealities, by introducing the chemical potential gradients as driving forces [27, 39]. When a multicomponent mixture with chemical reaction is considered, a hydrodynamic system which consists of the continuity equations for the constituents in the mixture and the MS equations, can be used to describe diffusion among the constituents and how their concentrations change as a consequence of the chemical reaction.

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Despite the practical interest and applications of the MS equations for multicomponent mixtures with or without chemical reaction, not much is known about the mathematical analysis of these equations. Rigorous results have been published over the past few years, see [8, 11, 12, 13, 21, 22, 23]. In particular, [12, 13, 22] dealt with the formal derivation of hydrodynamic systems of MS equations coupled with the continuity equations for the species from a kinetic (mesoscopic) system of Boltzmann equations for non-reactive multicomponent mixture and obtained explicit expressions for the diffusion coefficients in terms of the kinetic model parameters. Such papers follow the well established line of research initiated by Golse and co-workers [2, 3, 4] on the transition from kinetic Boltzmann models to hydrodynamic equations of fluid mechanics. In close connection with these works, but considering chemically reactive mixtures, we quote here [5, 6, 7] which dealt with the derivation of macroscopic reaction-diffusion equations from a system of reactive Boltzmann equations. In these papers, using an appropriate scaling of the reactive Boltzmann equations and assuming different types of molecular interactions, the evolution equations for the species number densities were explicitly derived in the asymptotic limit of small Knudsen number. Moreover, the convergence from the reactive Boltzmann equations to the reaction-diffusion system was proven and discussed in [5, 6]. Reaction-diffusion equations for chemically reactive mixtures were also derived in [33, 34, 40], starting from kinetic equations of Fokker-Planck type. Various scalings were considered in view of analyzing the interactions between transport processes and chemical reactions.

In the present paper, we are interested in the limiting process that leads from a particular model of reactive Boltzmann equations to a reaction-diffusion system of MS type. More precisely, we consider a quaternary mixture of monatomic ideal gases undergoing a bimolecular reversible reaction, described by the simple reacting sphere (SRS) kinetic model [30, 32, 38], in which both elastic and reactive collisions are of hard-sphere type. Then, considering a scaling of the SRS kinetic equations for which elastic collisions are dominant and reactive collisions are less frequent, and assuming isothermal condition, we formally derive the reaction-diffusion system of MS type from the evolution of the number density and momentum balance of the species. The formal derivation of these equations from a kinetic model is our main contribution in this paper and, as far as we know, this is the first attempt in this direction. Our assumptions correspond to a regime of slow, isothermal chemical reaction that occurs when the chemical process takes place at a rate slow enough to allow the surroundings to continuously compensate for the balance of reaction heat between the reactants and products [8, 9, 10, 21, 43, 44]. In the limit, we obtain a reaction diffusion system similar to those studied in [8, 9, 10]. If the isothermal assumption is disregarded, the evolution equation for the temperature of the mixture should be considered and the reaction diffusion system obtained in the limit will be similar to the one obtained in [42] for a non-reactive mixture.

After this introduction, the remaining part of our work is organized as follows. The reaction-diffusion system of MS type for a multi-species reactive mixture in the context of continuum mechanics is introduced in Section 2. In Section 3 we describe the SRS kinetic model and introduce its relevant properties that are essential for our analysis.

The diffusive asymptotics of the SRS kinetic model towards the reaction-diffusion system of MS type is studied in Section 4, after a proper scaling of the SRS equations. Our conclusions and some future perspectives are stated in Section 5. Finally, we include an Appendix in Section 6 where we give some steps and other details about the computation of the integrals appearing in Section 4.

2 The continuum reaction-diffusion system of Maxwell-Stefan type

In this section, we introduce a mathematical model for a reactive multi-species gaseous mixture in the context of continuum mechanics. The mixture is influenced by two processes, namely diffusion, which causes the species to spread in space, and chemical reaction, which results in the transformation of the species into each other. The model equations consist of the concentration balance equations for the reactive species in the mixture coupled with the MS equations for the momentum of the species. These equations describe how both processes affect the evolution of the mixture and will be referred to as the *reaction-diffusion system of MS type*.

Let $\Omega \subset \mathbb{R}^3$ be a bounded domain with boundary denoted by $\partial\Omega$ and outward normal vector at each point \mathbf{x} of the boundary given by $\nu(\mathbf{x})$. We consider a mixture of four species, say A_1, A_2, A_3 and A_4 , that participate in a chemical reaction of type



This means that species A_1, A_2 react to produce species A_3, A_4 and conversely, species A_3, A_4 also react to produce species A_1, A_2 . We say that A_1, A_2 and A_3, A_4 are the reactive species (or the reactive pairs), more specifically A_1, A_2 are reactants and A_3, A_4 are products of the forward chemical reaction. For each species A_i , with $i = 1, 2, 3, 4$, let $\varrho_i(t, \mathbf{x}) \geq 0$ be the mass density, $\mathbf{u}_i(t, \mathbf{x})$ the mean velocity and $r_i(t, \mathbf{x})$ the production rate of mass density due to the chemical reaction, where $\mathbf{x} \in \Omega$ and $t > 0$.

The mass balance equation for each constituent in the reactive mixture reads

$$\frac{\partial \varrho_i}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(\varrho_i \mathbf{u}_i) = r_i, \quad \mathbf{x} \in \Omega, \quad t > 0. \quad (2)$$

Due to the type of chemical reaction (1), the production rates satisfy the condition

$$\sum_{i=1}^4 r_i = 0, \quad (3)$$

which results in the conservation of the total mass of the mixture.

In this paper, we adopt a molar based description (see [16]) of the reactive mixture and, as a result, for each species A_i we introduce the molar mass M_i and define the molar concentration $c_i(t, \mathbf{x})$ and its production rate \mathcal{J}_i , the molar flux $\mathbf{N}_i(t, \mathbf{x})$, the mole fraction $\gamma_i(t, \mathbf{x})$ and the molar diffusive flux $\mathbf{J}_i(t, \mathbf{x})$, given respectively by

$$c_i = \frac{\varrho_i}{M_i}, \quad \mathcal{J}_i = \frac{r_i}{M_i}, \quad \mathbf{N}_i = c_i \mathbf{u}_i, \quad \gamma_i = \frac{c_i}{c}, \quad \mathbf{J}_i = c_i(\mathbf{u}_i - \mathbf{v}). \quad (4)$$

Here, $c := c(t, \mathbf{x})$ and $\mathbf{v} := \mathbf{v}(t, \mathbf{x})$ are the molar concentration and molar average velocity of the mixture, defined by

$$c = \sum_{i=1}^4 c_i, \quad \mathbf{v} = \sum_{i=1}^4 \gamma_i \mathbf{u}_i, \quad \mathbf{x} \in \Omega, \quad t > 0. \quad (5)$$

Note that the molar diffusive fluxes \mathbf{J}_i satisfy the constraint

$$\sum_{i=1}^4 \mathbf{J}_i = 0, \quad \mathbf{x} \in \Omega, \quad t > 0. \quad (6)$$

In our analysis, diffusion and chemical reaction are the relevant effects in the mixture. Therefore, as in [8, 9, 10, 21], we neglect the effects due to temperature gradients, by assuming an isothermal condition which corresponds to a uniform in space and constant in time mixture temperature T . We also neglect the effects due to convection and advection.

From the mass balance equation (2), using definitions (4), we obtain the evolution equations for the species concentrations c_i in the form

$$\frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{J}_i}{\partial \mathbf{x}} = \mathcal{J}_i, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \quad (7)$$

where we have considered $\frac{\partial}{\partial \mathbf{x}}(c_i \mathbf{v}) = \mathbf{0}$, since convection is neglected.

The diffusion process in multicomponent gaseous mixtures can be accurately described by the MS equations, which express the relationship between the molar diffusive fluxes and the chemical potentials of the species. Adopting the standard form for the chemical potentials [21] and taking into account the isothermal assumption, the driving forces (given by the chemical potentials) become equal to the concentration gradients of the species and the MS equations relate the molar diffusive fluxes to the concentration gradients. Following the description of [35], and using our notation, the MS equations under isobaric assumption (i.e. constant pressure) can be written in the form

$$\frac{\partial c_i}{\partial \mathbf{x}} = -\frac{1}{c} \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{D_{is}}, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \quad (8)$$

where D_{is} is the diffusion coefficient associated to species A_i and A_s , with $D_{is} = D_{si}$. Observe that summing (7) over all species as well as (8) over all species, we obtain

$$\frac{\partial c}{\partial t} = 0 \quad \text{and} \quad \frac{\partial c}{\partial \mathbf{x}} = 0,$$

which means that the total molar concentration of the mixture, c , is uniform in \mathbf{x} and constant in t . Also, the MS equations (8) are linearly dependent and only three of these equations are independent, so we have to add another equation to the system.

For what concerns the boundary conditions to join to our set of equations, we assume that the chemical reaction (1) takes place in a closed domain, so that we impose

$$\nu \cdot \mathbf{J}_i = 0, \quad \mathbf{x} \in \partial\Omega, \quad t > 0, \quad i = 1, 2, 3, 4. \quad (9)$$

Equations (7) and (8), together with constraint (6), constitute the reaction-diffusion system of MS type. These equations are similar to those studied in [8, 23]. They are used to describe diffusion and chemical kinetics of the multi-species reactive mixture in the context of continuum mechanics.

The aim of the present paper is to formally derive the balance equations (7) and the MS equations (8) as the hydrodynamic limit of the SRS kinetic model for the considered reactive mixture. The chemical production rates \mathcal{J}_i and the diffusion coefficients D_{is} will be explicitly computed from the collisional dynamics of the kinetic model and will be expressed in terms of some kinetic parameters.

3 The SRS kinetic model

In this section, we introduce our kinetic model for the quaternary reactive mixture considered in Section 2. This model is based on the kinetic theory of simple reacting spheres (SRS), first proposed by Marron in [28], and then developed by Xystriis, Dahler and Qin in [15, 32, 38]. Some aspects of the mathematical analysis of the SRS model were investigated, for example, in [14, 20, 29, 30]. Here, we introduce the model and briefly describe some of its properties needed for the analysis developed in this paper. Other details about the SRS model can be seen in the references just quoted above.

We consider the quaternary reactive mixture introduced in Section 2, whose constituents A_1, A_2, A_3, A_4 participate in the bimolecular chemical reaction (1) and confined ourselves to the simplifying assumption that the species are endowed with only translational degree of freedom. In other words, the species are monatomic like (i.e. internal degrees of freedom associated to rotational, vibrational and nuclei energies are not taken into account. For each $i = 1, 2, 3, 4$, let m_i , d_i and E_i be, respectively, the mass, the diameter and the formation energy of the species A_i . Conservation of mass holds for the chemical reaction (1) and thus we have

$$m_1 + m_2 = m_3 + m_4 = M. \quad (10)$$

The reaction heat, denoted by Q_R , is given by the difference between the formation energies of the products of the forward reaction and those of the reactants, i.e.

$$Q_R = E_3 + E_4 - E_1 - E_2. \quad (11)$$

This means that the forward reaction $A_1 + A_2 \rightarrow A_3 + A_4$ is exothermic if $Q_R < 0$. Otherwise, it is endothermic. Also, we introduce the activation energy ζ_i for each of the species A_i , such that $\zeta_1 = \zeta_2$, $\zeta_3 = \zeta_4$ and $\zeta_3 = \zeta_1 - Q_R$.

3.1 Collisional dynamics

Particles in the mixture undergo binary elastic collisions and reactive encounters obeying the chemical law (1), both of hard sphere type. Elastic collisions take place between particles of the same species, as well as between

particles of different species. The cross section of an elastic collision between particles of species A_i , A_s is defined by

$$\sigma_{is}^2 = \frac{1}{4}(d_i + d_s)^2, \quad i, s = 1, 2, 3, 4. \quad (12)$$

If $\mathbf{v}_i, \mathbf{v}_s$ are the pre-collisional velocities and $\mathbf{v}'_i, \mathbf{v}'_s$ the post-collisional velocities, the conservation laws of linear momentum and kinetic energy for elastic collisions are, respectively, given by

$$m_i \mathbf{v}_i + m_s \mathbf{v}_s = m_i \mathbf{v}'_i + m_s \mathbf{v}'_s \quad \text{and} \quad m_i (\mathbf{v}_i)^2 + m_s (\mathbf{v}_s)^2 = m_i (\mathbf{v}'_i)^2 + m_s (\mathbf{v}'_s)^2. \quad (13)$$

The post-collisional velocities are given in terms of the pre-collisional velocities by

$$\mathbf{v}'_i = \mathbf{v}_i - 2 \frac{\mu_{is}}{m_i} \epsilon \langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle \quad \text{and} \quad \mathbf{v}'_s = \mathbf{v}_s + 2 \frac{\mu_{is}}{m_s} \epsilon \langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle, \quad (14)$$

where

$$\mu_{is} = \frac{m_i m_s}{m_i + m_s} \quad (15)$$

is the reduced mass of the colliding pair, ϵ is a unit vector directed along the line joining the centre of the two spheres at the moment of impact, that is $\epsilon \in \mathbb{S}_+^2 = \{\bar{\epsilon} \in \mathbb{R}^3 : \|\bar{\epsilon}\| = 1, \langle \bar{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle > 0\}$. Moreover, $\langle \cdot, \cdot \rangle$ represents the inner product in \mathbb{R}^3 and $\|\cdot\|$ is the norm induced by this inner product. For convenience, we introduce the total mass of the colliding pair, $M_{is} = m_i + m_s$.

Remark 3.1 *Note that if we use spherical coordinates with $\theta \in [0, \pi/2]$ as the polar angle between $\mathbf{v}_i - \mathbf{v}_s$ and ϵ and $\phi \in [0, 2\pi[$ as the azimuthal angle in the plane orthogonal to $\mathbf{v}_i - \mathbf{v}_s$, then $\epsilon = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$. Also, $\langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle = V^* \cos \theta$, where $V^* = \|\mathbf{v}_i - \mathbf{v}_s\|$ is the norm of the relative velocity before collision.*

Concerning reactive encounters, a collision between particles of species A_i, A_j with pre-collisional velocities $\mathbf{v}_i, \mathbf{v}_j$ will result in a chemical reaction if the kinetic energy associated with the relative motion of the colliding pair along the line of their centres is greater than, or equal to, the activation energy, that is

$$\frac{1}{2} \mu_{ij} \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle^2 \geq \zeta_i. \quad (16)$$

If A_k, A_l represent the products of the forward reaction and $\mathbf{v}_k^\circ, \mathbf{v}_l^\circ$ their post-collisional velocities, then the conservation laws of linear momentum and total energy (kinetic plus binding) for reactive collisions are, respectively, given by

$$m_i \mathbf{v}_i + m_j \mathbf{v}_j = m_k \mathbf{v}_k^\circ + m_l \mathbf{v}_l^\circ, \quad (17)$$

$$E_i + \frac{1}{2} m_i (\mathbf{v}_i)^2 + E_j + \frac{1}{2} m_j (\mathbf{v}_j)^2 = E_k + \frac{1}{2} m_k (\mathbf{v}_k^\circ)^2 + E_l + \frac{1}{2} m_l (\mathbf{v}_l^\circ)^2, \quad (18)$$

where the indexes are such that $(i, j, k, l) \in \{(1, 2, 3, 4), (2, 1, 4, 3), (3, 4, 1, 2), (4, 3, 2, 1)\}$. From now on, if nothing is said about the indexes (i, j, k, l) , we assume that they are as introduced above.

Remark 3.2 *From condition (16), for a reactive collision to occur, we must have $\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle \geq \sqrt{2\zeta_i/\mu_{ij}}$. Using the definitions of the unit vector ϵ and relative velocity norm $V = \|\mathbf{v}_i - \mathbf{v}_j\|$ before the collision, we obtain $V \geq \sqrt{2\zeta_i/\mu_{ij}}$, which motivates the definition of the threshold relative velocity as $\Xi_{ij} = \sqrt{2\zeta_i/\mu_{ij}}$. In particular, Ξ_{ij} is the required relative velocity necessary to assure that the collision will be of reactive type.*

The reactive cross sections for the direct and reverse chemical reactions can be defined in terms of their threshold relative velocities by

$$\sigma_{12}^2 = \begin{cases} \beta_{12} \sigma_{12}^2, & \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle \geq \Xi_{12}, \\ 0, & \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle < \Xi_{12}, \end{cases} \quad \sigma_{34}^2 = \begin{cases} \beta_{34} \sigma_{34}^2, & \langle \epsilon, \mathbf{v}_3 - \mathbf{v}_4 \rangle \geq \Xi_{34}, \\ 0, & \langle \epsilon, \mathbf{v}_3 - \mathbf{v}_4 \rangle < \Xi_{34}, \end{cases} \quad (19)$$

where the coefficients β_{ij} represent the fraction of colliding pairs with enough kinetic energy to produce a reaction that in fact react chemically. They play the role of steric factors, with $0 \leq \beta_{ij} \leq 1$.

The post-collisional velocities for the forward chemical reaction $A_1 + A_2 \rightarrow A_3 + A_4$ are given by

$$\begin{aligned}\mathbf{v}_3^\circ &= \frac{1}{M} \left[m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2 + m_4 \sqrt{\frac{\mu_{12}}{\mu_{34}}} \{ (\mathbf{v}_1 - \mathbf{v}_2) - \epsilon \langle \epsilon, (\mathbf{v}_1 - \mathbf{v}_2) \rangle + \epsilon \omega^- \} \right], \\ \mathbf{v}_4^\circ &= \frac{1}{M} \left[m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2 - m_3 \sqrt{\frac{\mu_{12}}{\mu_{34}}} \{ (\mathbf{v}_1 - \mathbf{v}_2) - \epsilon \langle \epsilon, (\mathbf{v}_1 - \mathbf{v}_2) \rangle + \epsilon \omega^- \} \right],\end{aligned}\tag{20}$$

where $\omega^- = \sqrt{(\langle \epsilon, (\mathbf{v}_1 - \mathbf{v}_2) \rangle)^2 - 2Q_R/\mu_{12}}$. Analogously, the post-collisional velocities for the reverse chemical reaction $A_3 + A_4 \rightarrow A_1 + A_2$ are given by

$$\begin{aligned}\mathbf{v}_1^\circ &= \frac{1}{M} \left[m_3 \mathbf{v}_3 + m_4 \mathbf{v}_4 + m_2 \sqrt{\frac{\mu_{34}}{\mu_{12}}} \{ (\mathbf{v}_3 - \mathbf{v}_4) - \epsilon \langle \epsilon, (\mathbf{v}_3 - \mathbf{v}_4) \rangle + \epsilon \omega^+ \} \right], \\ \mathbf{v}_2^\circ &= \frac{1}{M} \left[m_3 \mathbf{v}_3 + m_4 \mathbf{v}_4 - m_1 \sqrt{\frac{\mu_{34}}{\mu_{12}}} \{ (\mathbf{v}_3 - \mathbf{v}_4) - \epsilon \langle \epsilon, (\mathbf{v}_3 - \mathbf{v}_4) \rangle + \epsilon \omega^+ \} \right],\end{aligned}\tag{21}$$

where $\omega^+ = \sqrt{(\langle \epsilon, (\mathbf{v}_3 - \mathbf{v}_4) \rangle)^2 + 2Q_R/\mu_{34}}$.

We close this subsection by recalling some properties about the dynamics of the reactive collisions that have been established in [14] and [30].

Property 3.3 *For a reactive collision, the following properties hold*

$$\frac{1}{2} \mu_{ij} (\mathbf{v}_i - \mathbf{v}_j)^2 = \frac{1}{2} \mu_{kl} (\mathbf{v}_k^\circ - \mathbf{v}_l^\circ)^2 + Q_R,\tag{22}$$

$$\mu_{ij} (\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle)^2 = \mu_{kl} (\langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle)^2 + 2Q_R,\tag{23}$$

$$\frac{1}{2} \mu_{ij} (\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle)^2 - \zeta_i = \frac{1}{2} \mu_{kl} (\langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle)^2 - \zeta_k,\tag{24}$$

$$\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle = \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{1}{2}} \omega^+.\tag{25}$$

Property 3.4 *For a fixed vector ϵ , the Jacobians of the transformations $(\mathbf{v}_i, \mathbf{v}_j) \mapsto (\mathbf{v}_k^\circ, \mathbf{v}_l^\circ)$ and $(\mathbf{v}_k, \mathbf{v}_l) \mapsto (\mathbf{v}_i^\circ, \mathbf{v}_j^\circ)$ are, respectively, given by*

$$\left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{3}{2}} \frac{\langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle}{\omega^+} \quad \text{and} \quad \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{3}{2}} \frac{\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle}{\omega^-}.\tag{26}$$

3.2 Kinetic equations

The state of the reactive mixture is described by the one-particle distribution functions $f_i(t, \mathbf{x}, \mathbf{v}_i)$ representing the density of particles of species A_i , expressed in moles, which at time t are located at position \mathbf{x} and have velocity \mathbf{v}_i , with $i = 1, 2, 3, 4$ and $(t, \mathbf{x}, \mathbf{v}_i) \in \mathbb{R}_+ \times \Omega \times \mathbb{R}^3$. The functions f_i are related to the molar concentrations c_i through the following expressions

$$c_i(t, \mathbf{x}) = \int_{\mathbb{R}^3} f_i(t, \mathbf{x}, \mathbf{v}_i) d\mathbf{v}_i, \quad t \geq 0, \quad \mathbf{x} \in \Omega, \quad i = 1, 2, 3, 4.\tag{27}$$

In absence of external forces, the SRS kinetic equations are given by

$$\frac{\partial f_i}{\partial t} + \mathbf{v}_i \cdot \frac{\partial f_i}{\partial \mathbf{x}} = J_i, \quad \text{in } \mathbb{R}_+ \times \Omega \times \mathbb{R}^3,\tag{28}$$

for $i = 1, 2, 3, 4$, with $J_i = J_i^E + J_i^R$, where J_i^E is the elastic collision operator and J_i^R is the reactive collision operator. They are respectively defined as follows,

$$\begin{aligned} J_i^E = & \sigma_{ii}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_{i*}' - f_i f_{i*}] \langle \epsilon, \mathbf{v}_i - \mathbf{v}_{i*} \rangle d\epsilon d\mathbf{v}_{i*} \\ & + \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_s' - f_i f_s] \langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle d\epsilon d\mathbf{v}_s \\ & - \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_j' - f_i f_j] \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j, \end{aligned} \quad (29)$$

$$J_i^R = \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 f_k^\circ f_l^\circ - f_i f_j \right] \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j, \quad (30)$$

where we have adopted the usual notation $f_i' = f(t, \mathbf{x}, \mathbf{v}_i')$, $f_{i*}' = f(t, \mathbf{x}, \mathbf{v}_{i*}')$, $f_s' = f(t, \mathbf{x}, \mathbf{v}_s')$, $f_k^\circ = f(t, \mathbf{x}, \mathbf{v}_k^\circ)$, $f_l^\circ = f(t, \mathbf{x}, \mathbf{v}_l^\circ)$, and Θ is a Heaviside step function, defined at $x \in \mathbb{R}$ by

$$\Theta(x) = \begin{cases} 1, & x \geq 0, \\ 0, & x < 0. \end{cases} \quad (31)$$

Equations (28) together with expressions (29) and (30) constitute the SRS kinetic system. Without being precise, the accompanying boundary conditions to describe the interactions between the molecules and the boundary $\partial\Omega$ of the evolution domain are taken to be of specular reflection type [37]. Such boundary conditions ensure that the reactive mixture is considered in a closed domain, as assumed in Section 2.

In expression (29) for the elastic collision operator, the first term on the right hand side represents collisions involving particles of the same species and the index i_* is used to distinguish their velocities. This term represents the standard Boltzmann collision operator for a single gas (mono-species) and will be denoted by J_i^{mE} . The second term in the same expression describes elastic collisions between particles of different species (bi-species) and will be denoted by J_i^{bE} . The last term singles out the fraction β_{ij} of those pre-collisional states that are energetic enough to result in chemical reaction, and thus prevent double counting of these collisions in the elastic and reactive operators. This term will be denoted by J_{ij}^{b*E} . Accordingly, in what follows, for $i = 1, 2, 3, 4$, we will write

$$J_i^E = J_i^{mE} + J_i^{bE} - J_{ij}^{b*E}, \quad (32)$$

with the following notations

$$J_i^{mE} = \sigma_{ii}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_{i*}' - f_i f_{i*}] \langle \epsilon, \mathbf{v}_i - \mathbf{v}_{i*} \rangle d\epsilon d\mathbf{v}_{i*}, \quad (33)$$

$$J_i^{bE} = \underbrace{\sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_s' - f_i f_s] \langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle d\epsilon d\mathbf{v}_s}_{\mathcal{Q}_{is}}, \quad (34)$$

$$J_{ij}^{b*E} = \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_j' - f_i f_j] \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j. \quad (35)$$

The following proposition provides an alternative form of writing the collision operator J_i , which is very useful to interpret the collisional dynamics of the model, in particular, the role of the operator J_{ij}^{b*E} . For the proof, it is enough to combine J_{ij}^{b*E} with the contribution from J_i^{bE} when $s = j$ and use the identity $\Theta(x) + \Theta(-x) = 1$.

Proposition 3.5 *For each $i = 1, 2, 3, 4$, the collision operator J_i introduced in (28) can be rewritten as*

$$J_i = \sigma_{ii}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_{i*}' - f_i f_{i*}] \langle \epsilon, \mathbf{v}_i - \mathbf{v}_{i*} \rangle d\epsilon d\mathbf{v}_{i*}$$

$$\begin{aligned}
& + \sigma_{ik}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_k' - f_i f_k] \langle \epsilon, \mathbf{v}_i - \mathbf{v}_k \rangle d\epsilon d\mathbf{v}_k + \sigma_{il}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_l' - f_i f_l] \langle \epsilon, \mathbf{v}_i - \mathbf{v}_l \rangle d\epsilon d\mathbf{v}_l \\
& + \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \Theta(\Xi_{ij} - \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle) [f_i' f_j' - f_i f_j] \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j \\
& + (1 - \beta_{ij}) \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) [f_i' f_j' - f_i f_j] \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j \\
& + \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 f_k^\circ f_l^\circ - f_i f_j \right] \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j.
\end{aligned} \tag{36}$$

Let us focus on the last three terms on the right hand side of expression (36), which are associated to collisions between the reactive species A_i and A_j . The first of these terms, with σ_{ij}^2 in front of it, is related to those collisions between A_i, A_j with insufficient amount of energy to produce a chemical reaction, and therefore are governed by elastic collisional dynamics. The last two terms correspond to collisions between A_i, A_j with sufficient amount of energy to produce a chemical reaction. However, only a fraction β_{ij} of such collisions results in a chemical reaction (last term) and produces species A_k and A_l . The remaining fraction $(1 - \beta_{ij})$ corresponds to collisions that are also governed by elastic collisional dynamics (second to the last term).

Remark 3.6 *Observe that by setting the coefficients β_{ij} equal to zero, the collisional terms J_i^{b*E} and J_i^R vanish, see (30) and (35). This corresponds to a situation in which the chemical reaction is turned off and we recover from our equations the hard-spheres model for a non-reactive mixture. Moreover, by setting the coefficients equal to one, all collisions with sufficient amount of energy to produce a chemical reaction will result, in fact, in a reactive collision. However, this is not the case in general, because it is well known in chemistry [41] that besides the activation energy barrier, the relative orientation of the molecules at the instant of collision is very important for the occurrence of a chemical reaction, meaning that only collisions with sufficient amount of energy and right orientation will result in a chemical reaction. Accordingly, we will consider in this paper the case in which $\beta_{ij} \in]0, 1[$ to guarantee that chemical reaction in fact occurs ($\beta_{ij} > 0$), but some collisions between the reactive species will not result in a chemical reaction due to improper orientation ($\beta_{ij} < 1$), even if they have enough energy to react chemically.*

3.3 Fundamental Properties of The SRS Model

In this subsection we review some fundamental properties of the SRS kinetic system. We have decided to include these properties in our paper because here we split the elastic collision operator in a particular form, see (32). These properties are adapted to our formalism and can be proved adapting the proofs in [14, 20, 29, 30] for similar results.

Lemma 3.7 *Given the mono-species elastic collision operator J_i^{mE} , let $\varphi(\mathbf{v}_i)$ be a sufficiently smooth test function. Then, the weak form of (33) for each of the species in the reactive mixture is given by*

$$\begin{aligned}
\int_{\mathbb{R}^3} J_i^{mE} \varphi(\mathbf{v}_i) d\mathbf{v}_i &= \frac{1}{4} \sigma_{ii}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_{i*}' - f_i f_{i*}] \langle \epsilon, \mathbf{v}_i - \mathbf{v}_{i*} \rangle \\
&\quad \times [\varphi(\mathbf{v}_i) + \varphi(\mathbf{v}_{i*}) - \varphi(\mathbf{v}_i') - \varphi(\mathbf{v}_{i*}')] d\epsilon d\mathbf{v}_{i*} d\mathbf{v}_i.
\end{aligned} \tag{37}$$

Lemma 3.8 *Given the bi-species elastic collision operator J_i^{bE} defined in (34) as a sum of several contributions of \mathcal{Q}_{is} , let $\varphi(\mathbf{v}_i)$ be a sufficiently smooth test function. Then, for each $i, s = 1, 2, 3, 4$ with $i \neq s$, we have that*

$$\int_{\mathbb{R}^3} \mathcal{Q}_{is} \varphi(\mathbf{v}_i) d\mathbf{v}_i = \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [\varphi(\mathbf{v}_i') - \varphi(\mathbf{v}_i)] f_i f_s \langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle d\epsilon d\mathbf{v}_s d\mathbf{v}_i. \tag{38}$$

Lemma 3.9 *Given the elastic collision operator J_{ij}^{b*E} defined in (35), let $\varphi(\mathbf{v}_i)$ be a sufficiently smooth test function. If we assume that $\beta_{ij} = \beta_{ji}$, then for $(i, j) \in \{(1, 2), (2, 1), (3, 4), (4, 3)\}$, we have that*

$$\int_{\mathbb{R}^3} J_{ij}^{b*E} \varphi(\mathbf{v}_i) d\mathbf{v}_i = \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [\varphi(\mathbf{v}'_i) - \varphi(\mathbf{v}_i)] f_i f_j \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \times \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i. \quad (39)$$

Concerning the reactive collision operator J_i^R , we have the following property.

Lemma 3.10 *Given the reactive collision operator J_i^R defined in (30), let $\varphi(\mathbf{v}_i)$ be a sufficiently smooth test function. If we assume that $\beta_{ij} = \beta_{ji}$ and $\beta_{12}\sigma_{12}^2 = \beta_{34}\sigma_{34}^2$, then we have that*

$$\begin{aligned} \sum_{i=1}^4 \int_{\mathbb{R}^3} J_i^R \varphi_i(\mathbf{v}_i) d\mathbf{v}_i &= \beta_{12} \sigma_{12}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [\varphi_1 + \varphi_2 - \varphi_3^\circ - \varphi_4^\circ] \left[\left(\frac{\mu_{12}}{\mu_{34}} \right)^2 f_3^\circ f_4^\circ - f_1 f_2 \right] \\ &\quad \times \Theta(\langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle - \Xi_{12}) \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle d\epsilon d\mathbf{v}_2 d\mathbf{v}_1 \\ &= \beta_{34} \sigma_{34}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [\varphi_3 + \varphi_4 - \varphi_1^\circ - \varphi_2^\circ] \left[\left(\frac{\mu_{34}}{\mu_{12}} \right)^2 f_1^\circ f_2^\circ - f_3 f_4 \right] \\ &\quad \times \Theta(\langle \epsilon, \mathbf{v}_3 - \mathbf{v}_4 \rangle - \Xi_{34}) \langle \epsilon, \mathbf{v}_3 - \mathbf{v}_4 \rangle d\epsilon d\mathbf{v}_4 d\mathbf{v}_3. \end{aligned} \quad (40)$$

3.4 Conservation equations

The conservation equations of the SRS model are obtained from the properties stated in Subsection 3.3. Their proofs are rather standard and follow the same line as in [14, 20, 29, 30].

Corollary 3.11 *The mono-species elastic collision operator given in (33) is such that, for $i = 1, 2, 3, 4$,*

$$\int_{\mathbb{R}^3} J_i^{mE} \begin{pmatrix} 1 \\ m_i \mathbf{v}_i \\ \frac{1}{2} m_i (\mathbf{v}_i)^2 \end{pmatrix} d\mathbf{v}_i = 0. \quad (41)$$

Proof. The proof follows from Lemma 3.7 and conservation laws (13). \square

Corollary 3.12 *Let \mathcal{Q}_{is} and J_{ij}^{b*E} be as defined in (34) and (35), respectively. Then*

$$\int_{\mathbb{R}^3} \mathcal{Q}_{is} d\mathbf{v}_i = 0, \quad (42)$$

$$\int_{\mathbb{R}^3} J_{ij}^{b*E} d\mathbf{v}_i = 0, \quad (43)$$

$$\int_{\mathbb{R}^3} \mathcal{Q}_{is} \begin{pmatrix} m_i \mathbf{v}_i \\ \frac{1}{2} m_i (\mathbf{v}_i)^2 \end{pmatrix} d\mathbf{v}_i + \int_{\mathbb{R}^3} \mathcal{Q}_{si} \begin{pmatrix} m_s \mathbf{v}_s \\ \frac{1}{2} m_s (\mathbf{v}_s)^2 \end{pmatrix} d\mathbf{v}_s = 0, \quad (44)$$

$$\int_{\mathbb{R}^3} J_{ij}^{b*E} \begin{pmatrix} m_i \mathbf{v}_i \\ \frac{1}{2} m_i (\mathbf{v}_i)^2 \end{pmatrix} d\mathbf{v}_i + \int_{\mathbb{R}^3} J_{ji}^{b*E} \begin{pmatrix} m_j \mathbf{v}_j \\ \frac{1}{2} m_j (\mathbf{v}_j)^2 \end{pmatrix} d\mathbf{v}_j = 0. \quad (45)$$

Proof. The proof follows from Lemmas 3.8, 3.9 and conservation laws (13). \square

Corollary 3.13 *The reactive collision operators satisfy the following property*

$$\int_{\mathbb{R}^3} J_1^R d\mathbf{v}_1 = \int_{\mathbb{R}^3} J_2^R d\mathbf{v}_2 = - \int_{\mathbb{R}^3} J_3^R d\mathbf{v}_3 = - \int_{\mathbb{R}^3} J_4^R d\mathbf{v}_4. \quad (46)$$

Proof. The proof follows from Lemma 3.10. □

Corollary 3.13 assures the correct exchange rates for the species in the chemical reaction (1).

Corollary 3.14 *The elastic and reactive collision operators are such that*

$$\sum_{i=1}^4 \int_{\mathbb{R}^3} \varphi(\mathbf{v}_i) (J_i^E + J_i^R) d\mathbf{v}_i = 0, \quad (47)$$

with $\varphi(\mathbf{v}_i)$ alternatively given by $\varphi(\mathbf{v}_i) = (1, 0, 1, 0)$, $\varphi(\mathbf{v}_i) = (1, 0, 0, 1)$, $\varphi(\mathbf{v}_i) = (0, 1, 1, 0)$, or by $\varphi(\mathbf{v}_i) = m_i v_{ix}$, $\varphi(\mathbf{v}_i) = m_i v_{iy}$, $\varphi(\mathbf{v}_i) = m_i v_{iz}$, or by $\varphi(\mathbf{v}_i) = E_i + \frac{1}{2} m_i \mathbf{v}_i^2$, where v_{ix} , v_{iy} and v_{iz} represent the spatial components of the molecular velocity \mathbf{v}_i .

Proof. The proof follows from Corollaries 3.11, 3.12 and Lemma 3.10. □

Corollary 3.14 indicates that, at least formally, the SRS model possesses seven independent macroscopic conservation laws, for the total number of particles of the reactant-product pairs of the form A_1 - A_3 , A_1 - A_4 and A_2 - A_3 , the three momentum components and the total energy of the mixture.

3.5 Equilibrium solutions and H-Theorem

The equilibrium solutions of the SRS system are characterized as follows.

Definition 3.15 *The equilibrium solutions of the SRS model (28) are distribution functions $f_i(t, \mathbf{x}, \mathbf{v}_i)$ such that the operators J_i^E and J_i^R given in (29) and (30) satisfy*

$$J_i^E + J_i^R = 0, \quad i = 1, \dots, 4. \quad (48)$$

Proposition 3.16 *If the coefficients β_{ij} and the reactive cross sections are such that $\beta_{ij} = \beta_{ji}$ and $\beta_{12}\sigma_{12}^2 = \beta_{34}\sigma_{34}^2$, then the following statements are equivalent*

$$(a) \ f_i = c_i \left(\frac{m_i}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{m_i (\mathbf{v}_i - \mathbf{u})^2}{2k_B T} \right), \text{ for } i = 1, \dots, 4, \text{ with}$$

$$c_1 c_2 = \left(\frac{\mu_{12}}{\mu_{34}} \right)^{1/2} c_3 c_4 \exp \left(\frac{Q_R}{k_B T} \right); \quad (49)$$

$$(b) \ J_i^E = 0 \text{ and } J_i^R = 0, \ i = 1, \dots, 4;$$

$$(c) \ \sum_{i=1}^4 \int_{\mathbb{R}^3} [J_i^E + J_i^R] \log \left(\frac{f_i}{\mu_{ij}} \right) dv = 0,$$

where

$$c_i(t, \mathbf{x}) = \int_{\mathbb{R}^3} f_i(t, \mathbf{x}, \mathbf{v}_i) d\mathbf{v}_i, \quad i = 1, \dots, 4, \quad (50a)$$

$$\mathbf{u}(t, \mathbf{x}) = \sum_{i=1}^4 \int_{\mathbb{R}^3} m_i \mathbf{v}_i f_i(t, \mathbf{x}, \mathbf{v}_i) d\mathbf{v}_i \Big/ \sum_{i=1}^4 \int_{\mathbb{R}^3} m_i f_i(t, \mathbf{x}, \mathbf{v}_i) d\mathbf{v}_i, \quad (50b)$$

$$T(t, \mathbf{x}) = \frac{1}{3k_B} \sum_{i=1}^4 \int_{\mathbb{R}^3} m_i (\mathbf{v}_i - \mathbf{u})^2 f_i(t, \mathbf{x}, \mathbf{v}_i) d\mathbf{v}_i \Big/ \sum_{i=1}^4 c_i(t, \mathbf{x}). \quad (50c)$$

Condition (49) represents the so called *mass action law* for the SRS kinetic model.

4 Reaction diffusion limit of the SRS kinetic model

In this section we formally derive the reaction-diffusion system of MS type as a hydrodynamic limit of the SRS kinetic model given in Section 3. In order to achieve this, we have to define an evolution regime for the chemical process and consider the mathematical assumptions that should be imposed on the kinetic model in agreement with the physical conditions associated to the MS setting.

4.1 The scaled equations and our assumptions

The starting point for the derivation of the reaction diffusion system of MS type is the scaled SRS kinetic system in a form compatible with the considered chemical regime of dominant elastic collisions and slow chemical reactions. Accordingly, we will consider the SRS kinetic equations written in non-dimensional form as

$$St \frac{\partial \hat{f}_i}{\partial t} + \hat{\mathbf{v}}_i \cdot \frac{\partial \hat{f}_i}{\partial \hat{\mathbf{x}}} = \frac{1}{Kn_e} \hat{J}_i^{mE} + \frac{1}{Kn_e} \hat{J}_i^{bE} - \frac{1}{Kn_r} \hat{J}_{ij}^{b*E} + \frac{1}{Kn_r} \hat{J}_i^R, \quad i = 1, 2, 3, 4, \quad (51)$$

where St is the kinetic Strouhal number [19], Kn_e and Kn_r are the elastic and reactive Knudsen numbers [1]. The Knudsen numbers are such that the reactive and elastic mean free paths are related by the factor $Kn_r/Kn_e = 1/\beta_{ij}$. The symbols with the hat indicate scaled quantities with respect to a reference length L , time τ and temperature T_0 . We also introduce the speed of sound c_0 in a mixture of monatomic ideal gases at temperature T_0 , given by $c_0 = \sqrt{\frac{5n_0 k_B T_0}{3\rho_0}}$, and scale the velocities with respect to c_0 . The scaled collisional operators are defined by

$$\begin{aligned} \hat{J}_i^{mE} &= \hat{\sigma}_{ii}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [\hat{f}_i' \hat{f}_{i*}' - \hat{f}_i \hat{f}_{i*}] \langle \epsilon, \hat{\mathbf{v}}_i - \hat{\mathbf{v}}_{i*} \rangle d\epsilon d\hat{\mathbf{v}}_{i*}, \\ \hat{J}_i^{bE} &= \sum_{\substack{s=1 \\ s \neq i}}^4 \hat{\sigma}_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [\hat{f}_i' \hat{f}_s' - \hat{f}_i \hat{f}_s] \langle \epsilon, \hat{\mathbf{v}}_i - \hat{\mathbf{v}}_s \rangle d\epsilon d\hat{\mathbf{v}}_s, \\ \hat{J}_{ij}^{b*E} &= \hat{\sigma}_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [\hat{f}_i' \hat{f}_j' - \hat{f}_i \hat{f}_j] \Theta(\langle \epsilon, c_0 \hat{\mathbf{v}}_i - c_0 \hat{\mathbf{v}}_j \rangle - \Xi_{ij}) \langle \epsilon, \hat{\mathbf{v}}_i - \hat{\mathbf{v}}_j \rangle d\epsilon d\hat{\mathbf{v}}_j, \\ \hat{J}_i^R &= \hat{\sigma}_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 \hat{f}_k^\circ \hat{f}_l^\circ - \hat{f}_i \hat{f}_j \right] \Theta(\langle \epsilon, c_0 \hat{\mathbf{v}}_i - c_0 \hat{\mathbf{v}}_j \rangle - \Xi_{ij}) \langle \epsilon, \hat{\mathbf{v}}_i - \hat{\mathbf{v}}_j \rangle d\epsilon d\hat{\mathbf{v}}_j. \end{aligned}$$

Moreover, we assume that the bulk velocity of the mixture is comparable to L/τ and, as a result, the Strouhal number becomes the Mach number, Ma . Henceforth, we introduce the notations

$$St = Ma = \alpha, \quad Kn_e = \alpha^p \quad \text{and} \quad Kn_r = \alpha^q, \quad (52)$$

where $\alpha \ll 1$, p and q are real numbers with $p \geq 1$ and $p > q$. Also, we assume that the elastic Knudsen number is of the same order of magnitude as the Mach number, so that $p = 1$. Additionally, we are interested in a chemical regime for which elastic collisions are predominant and reactive collisions are rare, so that we assume

$q = -1$. Using the above notations and the generic assumptions in (51), and removing the hats for simplicity, we obtain that, for $i = 1, 2, 3, 4$,

$$\alpha \frac{\partial f_i^\alpha}{\partial t} + \mathbf{v}_i \cdot \frac{\partial f_i^\alpha}{\partial \mathbf{x}} = \frac{1}{\alpha} J_i^{m\alpha E} + \frac{1}{\alpha} J_i^{b\alpha E} - \alpha J_{ij}^{b*\alpha E} + \alpha J_i^{\alpha R}, \quad \text{in } \mathbb{R}_+ \times \Omega \times \mathbb{R}^3, \quad (53)$$

where f_i^α , $i = 1, 2, 3, 4$, are now the scaled unknowns in the considered regime and $J_i^{m\alpha E}$, $J_i^{b\alpha E}$, $J_{ij}^{b*\alpha E}$, $J_i^{\alpha R}$ indicate that the collisional operators are now expressed in terms of f_i^α . Equations (53) emphasize that the mono-species and bi-species elastic operators $J_i^{m\alpha E}$ and $J_i^{b\alpha E}$ are associated to predominant effects, whereas the reactive operator $J_i^{\alpha R}$ and the correction elastic term $J_{ij}^{b*\alpha E}$ are associated to rare effects.

With the obvious adjustments, the conservation laws and properties of the SRS model given in Section 3 are still valid for the scaled equations (53).

Besides the chemical regime of slow chemical reaction, our central assumptions to derive the reaction diffusion system of MS type from the kinetic formulation are as follows:

- (a) The initial conditions are local Maxwellian functions centred at the mean velocity of the species.
- (b) The evolution of the system leaves the distribution functions in the local Max-wellian state.
- (c) The bulk velocity of the mixture is small and goes to zero as $\alpha \rightarrow 0$.
- (d) The evolution of the mixture obeys the isothermal condition.

Assumption (d) implies that the temperature T of the mixture is uniform in space and constant in time. It is compatible with the physical situation of slow chemical reaction and signifies that the chemical process takes place at a rate slow enough to allow the surroundings to continuously compensate for the balance of reaction heat between the reactants and products (see [43]). Assumption (c) allows us to neglect convective effects and describe a physical system governed by diffusion and chemical reaction. Assumptions (a) and (b) correspond to the physical situation in which the system evolves not far away from the local Maxwellian equilibrium.

From both the assumption (a) and the first assertion of (52), and following [18, 19], the initial conditions for (53) are distribution functions of the following form

$$f_i^{\alpha(in)}(\mathbf{x}, \mathbf{v}_i) = c_i^{\alpha(in)}(\mathbf{x}) \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left[-\frac{m_i \left(\mathbf{v}_i - \alpha \mathbf{u}_i^{\alpha(in)}(\mathbf{x}) \right)^2}{2k_B T} \right], \quad \mathbf{x} \in \Omega, \quad \mathbf{v}_i \in \mathbb{R}^3, \quad (54)$$

where $T > 0$ is constant (isothermal condition), $c_i^{\alpha(in)} : \Omega \rightarrow \mathbb{R}_+$, for $i = 1, \dots, 4$, with $c^{\alpha(in)} = \sum_{i=1}^4 c_i^{\alpha(in)}$, and $\mathbf{u}_i^{\alpha(in)} : \Omega \rightarrow \mathbb{R}^3$, for $i = 1, \dots, 4$. From assumption (b), the distribution functions at time $t > 0$ are local Maxwellians centred at the mean velocity of the species, given by

$$f_i^\alpha(t, \mathbf{x}, \mathbf{v}_i) = c_i^\alpha(t, \mathbf{x}) \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left[-\frac{m_i \left(\mathbf{v}_i - \alpha \mathbf{u}_i^\alpha(t, \mathbf{x}) \right)^2}{2k_B T} \right], \quad \mathbf{x} \in \Omega, \quad \mathbf{v}_i \in \mathbb{R}^3, \quad (55)$$

where $c_i^\alpha : \mathbb{R}_+ \times \Omega \rightarrow \mathbb{R}_+$ and $\mathbf{u}_i^\alpha : \mathbb{R}_+ \times \Omega \rightarrow \mathbb{R}^3$, for $i = 1, \dots, 4$. Using (55), the moments of order 0 and 1 of the distribution functions are, respectively, given by

$$\int_{\mathbb{R}^3} f_i^\alpha(t, \mathbf{x}, \mathbf{v}_i) d\mathbf{v}_i = c_i^\alpha(t, \mathbf{x}) \quad \text{and} \quad \int_{\mathbb{R}^3} \mathbf{v}_i f_i^\alpha(t, \mathbf{x}, \mathbf{v}_i) d\mathbf{v}_i = \alpha c_i^\alpha(t, \mathbf{x}) \mathbf{u}_i^\alpha(t, \mathbf{x}). \quad (56)$$

An important step in the passage from a kinetic model to hydrodynamic equations is the explicit computation of the integral contributions appearing in the kinetic equations. When a reactive mixture is involved, such computation can be very intricate, essentially because of the redistribution of masses and internal energies

among the constituents. Having this in mind, in the light of assumption (c), the Maxwellian (55) with species velocity will be approximated through a first order expansion around the Maxwellian M_i^α with a common and vanishing mixture velocity, namely

$$f_i^\alpha(t, \mathbf{x}, \mathbf{v}_i) \approx M_i^\alpha(t, \mathbf{x}, \mathbf{v}_i) \left[1 + \frac{\alpha m_i \mathbf{v}_i \cdot \mathbf{u}_i^\alpha(t, \mathbf{x})}{k_B T} \right], \quad (57)$$

with

$$M_i^\alpha(t, \mathbf{x}, \mathbf{v}_i) = c_i^\alpha(t, \mathbf{x}) \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \exp\left(-\frac{m_i (\mathbf{v}_i)^2}{2k_B T} \right). \quad (58)$$

Expressions (57) will be used in Subsections 4.2 and 4.3 for the explicit computation of the integral contributions. As stated by Present in [31], p. 147, first-order corrections to the Maxwellian distributions (58) as those given by expansions (57) were first used by J. Stefan in his celebrated work from 1872 to capture the diffusion effects in a mixture of gases.

Moreover, hereinafter we will use the notation $\Gamma(\eta, x)$ for the incomplete Euler gamma function defined by

$$\Gamma(\eta, x) = \int_x^\infty t^{\eta-1} e^{-t} dt. \quad (59)$$

4.2 Concentration balance equations

The balance equations for the species concentration can formally be derived from the scaled SRS equations given in (53), by integrating over the velocity space. Also, the conservation laws and some of the fundamental properties of the kinetic model stated in Section 3 will be used to achieve the following result.

Lemma 4.1 *The concentration balance equations for the species in the reactive mixture can be written as*

$$\frac{\partial c_i^\alpha}{\partial t} + \frac{\partial}{\partial \mathbf{x}} (c_i^\alpha \mathbf{u}_i^\alpha) = \mathcal{J}_i, \quad i = 1, \dots, 4, \quad (60)$$

with \mathcal{J}_i being the reaction rate of the i -th species given by

$$\begin{aligned} \mathcal{J}_i = \sigma_{ij}^2 \left(\frac{2\pi\mu_{ij}}{k_B T} \right)^{\frac{1}{2}} & \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T} \right) - c_i^\alpha c_j^\alpha \right] \\ & \times \left[\frac{2k_B T}{\mu_{ij}} \Gamma(2, z_i^*) - \left(\frac{\Xi_{ij}}{c_0} \right)^2 \Gamma(1, z_i^*) \right], \end{aligned} \quad (61)$$

where the terms $\Gamma(1, z_i^*)$, $\Gamma(2, z_i^*)$ are defined by (59) with

$$z_i^* = \frac{\mu_{ij}}{2k_B T} \left(\frac{\Xi_{ij}}{c_0} \right)^2. \quad (62)$$

Moreover, for each $i = 1, \dots, 4$ we have $\mathcal{J}_i = \lambda_i \mathcal{J}_1$, with $\lambda_1 = \lambda_2 = 1$ and $\lambda_3 = \lambda_4 = -1$.

Proof. First, we integrate both sides of the scaled SRS equations given in (53) with respect to $\mathbf{v}_i \in \mathbb{R}^3$, to obtain

$$\alpha \frac{\partial}{\partial t} \left(\int_{\mathbb{R}^3} f_i^\alpha d\mathbf{v}_i \right) + \frac{\partial}{\partial \mathbf{x}} \left(\int_{\mathbb{R}^3} \mathbf{v}_i f_i^\alpha d\mathbf{v}_i \right) = \alpha \int_{\mathbb{R}^3} J_i^{\alpha R} d\mathbf{v}_i,$$

where we have used Corollary 3.11, Lemma 3.8 with $\varphi(\mathbf{v}_i) = 1$, and Lemma 3.9 with $\varphi(\mathbf{v}_i) = 1$. Using (56), we obtain

$$\frac{\partial c_i^\alpha}{\partial t} + \frac{\partial}{\partial \mathbf{x}} (c_i^\alpha \mathbf{u}_i^\alpha) = \int_{\mathbb{R}^3} J_i^{\alpha R} d\mathbf{v}_i. \quad (63)$$

Next, we derive an explicit expression for the integral contribution on the right hand side of (63). To do this, we replace the distribution functions by their approximations (57). For sake of simplicity, we write such approximations in the form

$$f_i^\alpha \approx M_i^\alpha (1 + \mathbf{a}_i \cdot \mathbf{v}_i), \quad \text{with} \quad \mathbf{a}_i = \frac{\alpha m_i \mathbf{u}_i^\alpha}{k_B T}, \quad (64)$$

and, for any index i , we refer to \mathbf{a}_i as coefficient \mathbf{a} . Using (64), we can write the integral on the right-hand-side of (63) as the sum of the following three terms,

$$\begin{aligned} \mathcal{D} &= \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left(\frac{\mu_{ij}^2}{\mu_{kl}^2} M_k^{\alpha\circ} M_l^{\alpha\circ} - M_i^\alpha M_j^\alpha \right) \Theta(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i, \\ \mathcal{E} &= \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left(\frac{\mu_{ij}^2}{\mu_{kl}^2} M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ + \mathbf{a}_l \cdot \mathbf{v}_l^\circ) \right) \Theta(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i, \\ \mathcal{F} &= -\sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left(M_i^\alpha M_j^\alpha (\mathbf{a}_i \cdot \mathbf{v}_i + \mathbf{a}_j \cdot \mathbf{v}_j) \right) \Theta(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i, \end{aligned} \quad (65)$$

where quadratic terms in the coefficients \mathbf{a} have been neglected.

Inserting (58) into the integral contributions \mathcal{D} , \mathcal{E} and \mathcal{F} , we obtain

- (i) $\mathcal{D} = \mathcal{J}_i$, with \mathcal{J}_i the reaction rate defined in (61);
- (ii) $\mathcal{E} = 0$;
- (iii) $\mathcal{F} = 0$.

Concerning items (ii) and (iii), the computations require some variable transformations and we give some details in Appendix A of Subsection 6.1. Let us focus on item (i). Using (58) and the conservation law of total energy during reactive collisions given in (18), we obtain

$$\begin{aligned} \mathcal{D} &= \sigma_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T}\right) - c_i^\alpha c_j^\alpha \right] \\ &\quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \exp\left[-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T}\right] \Theta(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i. \end{aligned} \quad (66)$$

Evaluating the integral over \mathbb{S}_+^2 , using spherical coordinates as described in Remark 3.1, we obtain

$$\int_{\mathbb{S}_+^2} \Theta(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon = \pi V \Theta\left(V - \frac{\Xi_{ij}}{c_0}\right) \left[1 - \left(\frac{\Xi_{ij}}{c_0 V}\right)^2\right]. \quad (67)$$

Substituting (67) into (66), then transforming the resulting sixfold integral in $\mathbf{v}_i, \mathbf{v}_j$ to the relative velocity $\mathbf{V} = \mathbf{v}_j - \mathbf{v}_i$ and centre of mass velocity $\mathbf{X} = (m_i \mathbf{v}_i + m_j \mathbf{v}_j)/(m_i + m_j)$, and using the fact that the Jacobian of the transformation has absolute value 1, we get

$$\begin{aligned} \mathcal{D} &= \pi \sigma_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T}\right) - c_i^\alpha c_j^\alpha \right] \\ &\quad \times \int_{\mathbb{R}^3} \exp\left(-\frac{M X^2}{2k_B T}\right) d\mathbf{X} \int_{\mathbb{R}^3} V \Theta\left(V - \frac{\Xi_{ij}}{c_0}\right) \left[1 - \left(\frac{\Xi_{ij}}{c_0 V}\right)^2\right] \exp\left(-\frac{\mu_{ij} V^2}{2k_B T}\right) d\mathbf{V}, \end{aligned} \quad (68)$$

where $M = m_i + m_j$. The integral in \mathbf{X} can be easily evaluated and becomes

$$\int_{\mathbb{R}^3} \exp\left(-\frac{MX^2}{2k_B T}\right) d\mathbf{X} = \left(\frac{2\pi k_B T}{M}\right)^{\frac{3}{2}}. \quad (69)$$

The integral in \mathbf{V} can be expanded and the resulting terms are computed by first transforming to spherical coordinates. Next, the resulting scalar integrals in V are transformed to z , using $z = \frac{\mu_{ij}}{2k_B T} V^2$, and finally using (59), we obtain

$$\begin{aligned} \int_{\mathbb{R}^3} V \Theta\left(V - \frac{\Xi_{ij}}{c_0}\right) \exp\left(-\frac{\mu_{ij} V^2}{2k_B T}\right) d\mathbf{V} - \int_{\mathbb{R}^3} V \exp\left(-\frac{\mu_{ij} V^2}{2k_B T}\right) \Theta\left(V - \frac{\Xi_{ij}}{c_0}\right) \left(\frac{\Xi_{ij}}{c_0 V}\right)^2 d\mathbf{V} \\ = 2\pi \frac{2k_B T}{\mu_{ij}} \left[\frac{2k_B T}{\mu_{ij}} \Gamma(2, z_i^*) - \left(\frac{\Xi_{ij}}{c_0}\right)^2 \Gamma(1, z_i^*) \right]. \end{aligned} \quad (70)$$

Substituting (69) and (70) into (68), and performing a little algebra, we obtain the desired expression (61) for the integral \mathcal{D} in item (i).

The last assertion of Lemma 4.1 is an immediate consequence of Corollary 3.13 about the reactive collision operators. \square

Remark 4.2 (a) The reaction rate \mathcal{J}_i given in (61) can be written in an equivalent form, as a phenomenological law for the chemical reaction (1), as

$$\mathcal{J}_i = -\lambda_i \left(k_f c_1^\alpha c_2^\alpha - k_b c_3^\alpha c_4^\alpha \right), \quad i = 1, \dots, 4, \quad (71)$$

with k_f and k_b being the forward and backward rate constants given, respectively, by

$$k_f = \sigma_{12}^2 \sqrt{\frac{8\pi k_B T}{\mu_{12}}} \exp\left(-\frac{\zeta_1}{k_B T}\right) \quad \text{and} \quad k_b = \sigma_{34}^2 \sqrt{\frac{8\pi k_B T}{\mu_{34}}} \exp\left(-\frac{\zeta_3}{k_B T}\right), \quad (72)$$

Equation (71) expresses the reaction rate in the form used, in general, in physical applications, see [24].

(b) Our expression (61) differs from the corresponding one obtained in paper [5], see (42) in that paper, essentially because the SRS reactive cross sections are of hard-sphere type and the integral over \mathbb{S}_+^2 is explicitly evaluated in (67), whereas reactive cross sections in paper [5] are of Maxwell molecules type and the integral over \mathbb{S}_+^2 is not explicitly evaluated. Moreover, our exponent $1/2$, instead of $3/2$ as in paper [5], is a consequence of the fact that the exponent of the term (μ_{ij}/μ_{kl}) in our reactive collision operator J_i^R is 2, see (30), while in [5] it is 3.

4.3 Momentum balance equation

The momentum balance equations for the species in the reactive mixture can formally be derived from the scaled equations (53), after multiplying by the molecular velocity \mathbf{v}_i and then integrating over the velocity space. Also, the conservation laws and some of the fundamental properties stated in Section 3 will be used to compute explicitly the production terms appearing in the balance equations.

However, some words are needed before presenting the next lemma. As it is well known, the computation of the integral contributions appearing in the momentum balance equations is rather technical and extremely intricate, and the final explicit expressions of these contributions are quite huge. On the other hand, as it will become clear from the balance equations derived in the lemma (see (73), below), only the $O(1)$ terms in α will be retained in the equations, that is only those terms associated to the elastic scattering will influence the final formulation of the balance equations. Accordingly, we include in the next lemma only the explicit expressions of the $O(1)$ terms and present in Appendix 6.2 the explicit expression of the $O(\alpha^2)$ terms.

Lemma 4.3 *The momentum balance equation for each of the species in the reactive mixture is given by*

$$\alpha^2 \frac{\partial}{\partial t} (c_i^\alpha \mathbf{u}_i^\alpha) + \frac{k_B T}{m_i} \frac{\partial c_i^\alpha}{\partial \mathbf{x}} + \alpha^2 \frac{\partial}{\partial \mathbf{x}} (c_i^\alpha \mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha) = \mathcal{O}_i - \mathcal{P}_i + \mathcal{Q}_i, \quad (73)$$

where \mathcal{O}_i is an $O(1)$ production term associated to the elastic scattering, and is given by

$$\mathcal{O}_i = \frac{1}{\alpha} \int_{\mathbb{R}^3} \mathbf{v}_i J_i^{b\alpha E} d\mathbf{v}_i = \frac{32}{9} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} \left(\frac{2\pi k_B T}{\mu_{is}} \right)^{\frac{1}{2}} c_i^\alpha c_s^\alpha (\mathbf{u}_s^\alpha - \mathbf{u}_i^\alpha), \quad (74)$$

and $\mathcal{P}_i, \mathcal{Q}_i$ are $O(\alpha^2)$ production terms associated to the chemical process, and are respectively given by

$$\mathcal{P}_i = \alpha \int_{\mathbb{R}^3} \mathbf{v}_i J_{ij}^{b\alpha * E} d\mathbf{v}_i, \quad \mathcal{Q}_i = \alpha \int_{\mathbb{R}^3} \mathbf{v}_i J_i^{\alpha R} d\mathbf{v}_i, \quad (75)$$

whose explicit expressions are given in Appendix 6.2, see (91) and (104).

Proof. First, we multiply both sides of the scaled SRS equations given in (53) by \mathbf{v}_i and integrate with respect $\mathbf{v}_i \in \mathbb{R}^3$, to obtain

$$\begin{aligned} \alpha \frac{\partial}{\partial t} \left(\int_{\mathbb{R}^3} \mathbf{v}_i f_i^\alpha d\mathbf{v}_i \right) + \frac{\partial}{\partial \mathbf{x}} \left(\int_{\mathbb{R}^3} \mathbf{v}_i \otimes \mathbf{v}_i f_i^\alpha d\mathbf{v}_i \right) &= \frac{1}{\alpha} \int_{\mathbb{R}^3} \mathbf{v}_i J_i^{m\alpha E} d\mathbf{v}_i \\ &+ \underbrace{\frac{1}{\alpha} \int_{\mathbb{R}^3} \mathbf{v}_i J_i^{b\alpha E} d\mathbf{v}_i}_{\mathcal{O}_i} - \underbrace{\alpha \int_{\mathbb{R}^3} \mathbf{v}_i J_{ij}^{b*\alpha E} d\mathbf{v}_i}_{\mathcal{P}_i} + \underbrace{\alpha \int_{\mathbb{R}^3} \mathbf{v}_i J_i^{\alpha R} d\mathbf{v}_i}_{\mathcal{Q}_i}. \end{aligned} \quad (76)$$

Let us concentrate first on the left-hand-side terms in (76).

(i) From the second expression in (56), it immediately follows that

$$\alpha \frac{\partial}{\partial t} \left(\int_{\mathbb{R}^3} \mathbf{v}_i f_i^\alpha d\mathbf{v}_i \right) = \alpha^2 \frac{\partial}{\partial t} (c_i^\alpha \mathbf{u}_i^\alpha). \quad (77)$$

(ii) For what concerns the second term on the left-hand side of (76), we transform from \mathbf{v}_i to the peculiar velocity $\boldsymbol{\xi}_i = \mathbf{v}_i - \alpha \mathbf{u}_i^\alpha$ and then use the fact that the Jacobian of the transformation is equal to 1 to obtain

$$\begin{aligned} \frac{\partial}{\partial \mathbf{x}} \left(\int_{\mathbb{R}^3} \mathbf{v}_i \otimes \mathbf{v}_i f_i^\alpha d\mathbf{v}_i \right) &= \frac{\partial}{\partial \mathbf{x}} \left(\int_{\mathbb{R}^3} f_i^\alpha \boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i d\boldsymbol{\xi}_i \right) + 2\alpha \frac{\partial}{\partial \mathbf{x}} \left(\mathbf{u}_i^\alpha \otimes \int_{\mathbb{R}^3} f_i^\alpha \boldsymbol{\xi}_i d\boldsymbol{\xi}_i \right) \\ &+ \alpha^2 \frac{\partial}{\partial \mathbf{x}} \left(\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha \int_{\mathbb{R}^3} f_i^\alpha d\boldsymbol{\xi}_i \right). \end{aligned} \quad (78)$$

Inserting (55), expressed in terms of the peculiar velocity $\boldsymbol{\xi}_i$, into (78) and evaluating the integrals, we easily see that the second term on the right hand side vanishes. Consequently, (78) reduces to

$$\frac{\partial}{\partial \mathbf{x}} \left(\int_{\mathbb{R}^3} \mathbf{v}_i \otimes \mathbf{v}_i f_i^\alpha d\mathbf{v}_i \right) = \frac{k_B T}{m_i} \frac{\partial c_i^\alpha}{\partial \mathbf{x}} + \alpha^2 \frac{\partial}{\partial \mathbf{x}} (c_i^\alpha \mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha). \quad (79)$$

Now let us deal with the terms on the right hand side of (76).

(iii) The first term vanishes by virtue of the second assertion in Corollary 3.11 about the mono-species elastic operator, see (41).

(iv) To derive an explicit expression for the production term \mathcal{O}_i , we use the considered approximation of f_i^α in the form (57) or (64). Taking into account Lemma 3.8 with $\varphi(\mathbf{v}'_i) = \mathbf{v}'_i$ and $\varphi(\mathbf{v}_i) = \mathbf{v}_i$, we obtain

$$\mathcal{O}_i = \frac{1}{\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{v}'_i - \mathbf{v}_i) f_i^\alpha f_s^\alpha \langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle d\epsilon d\mathbf{v}_s d\mathbf{v}_i.$$

Using the first expression in (14) for \mathbf{v}'_i , evaluating the integral over the sphere \mathbb{S}_+^2 by transforming to spherical coordinates as described in Remark 3.1, and transforming the remaining sixfold integral in \mathbf{v}_i and \mathbf{v}_s to the relative velocity $\mathbf{V}^* = \mathbf{v}_s - \mathbf{v}_i$ and centre of mass velocity $\mathbf{X}^* = (m_i \mathbf{v}_i + m_s \mathbf{v}_s)/M_{is}$, with $M_{is} = m_i + m_s$, as defined before, we obtain

$$\begin{aligned} \mathcal{O}_i = & \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{M_{is}} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \\ & \times \left\{ \left(\int_{\mathbb{R}^3} \exp\left(-\frac{M_{is} X^{*2}}{2k_B T}\right) d\mathbf{X}^* \right) \left(\int_{\mathbb{R}^3} V^* \exp\left(-\frac{\mu_{is} V^{*2}}{2k_B T}\right) \mathbf{V}^* d\mathbf{V}^* \right) \right. \\ & + \left(\int_{\mathbb{R}^3} \exp\left(-\frac{M_{is} X^{*2}}{2k_B T}\right) \mathbf{X}^* d\mathbf{X}^* \right) (\mathbf{a}_s + \mathbf{a}_i) \cdot \left(\int_{\mathbb{R}^3} V^* \exp\left(-\frac{\mu_{is} V^{*2}}{2k_B T}\right) \mathbf{V}^* d\mathbf{V}^* \right) \\ & + \frac{m_i}{M_{is}} \left(\int_{\mathbb{R}^3} \exp\left(-\frac{M_{is} X^{*2}}{2k_B T}\right) d\mathbf{X}^* \right) \left(\int_{\mathbb{R}^3} (\mathbf{a}_s \cdot \mathbf{V}^*) \mathbf{V}^* \exp\left(-\frac{\mu_{is} V^{*2}}{2k_B T}\right) V^* d\mathbf{V}^* \right) \\ & \left. - \frac{m_s}{M_{is}} \left(\int_{\mathbb{R}^3} \exp\left(-\frac{M_{is} X^{*2}}{2k_B T}\right) d\mathbf{X}^* \right) \left(\int_{\mathbb{R}^3} (\mathbf{a}_i \cdot \mathbf{V}^*) \mathbf{V}^* \exp\left(-\frac{\mu_{is} V^{*2}}{2k_B T}\right) V^* d\mathbf{V}^* \right) \right\}, \end{aligned} \quad (80)$$

where we have neglected the quadratic term in the coefficients \mathbf{a} and introduced the notation $V^* = \|\mathbf{V}^*\|$, $X^* = \|\mathbf{X}^*\|$. Also, $\mathbf{a}_i = \frac{\alpha m_i \mathbf{u}_i^\alpha}{k_B T}$, $\mathbf{a}_s = \frac{\alpha m_s \mathbf{u}_s^\alpha}{k_B T}$ as defined in (64).

Considering the first integral in (80), writing $\mathbf{V}^* = V^* \vec{\mathbf{v}}$ with $\vec{\mathbf{v}}$ a unit vector, and transforming to spherical coordinates, we conclude that the integral vanishes, since

$$\begin{aligned} \int_{\mathbb{R}^3} V^* \exp\left(-\frac{\mu_{is} V^{*2}}{2k_B T}\right) \mathbf{V}^* d\mathbf{V}^* = & \int_0^\infty V^{*4} \exp\left(-\frac{\mu_{is} V^{*2}}{2k_B T}\right) dV^* \left(\int_0^\pi \sin^2 \theta d\theta \int_0^{2\pi} \cos \phi d\phi \hat{\mathbf{x}} \right. \\ & \left. + \int_0^\pi \sin^2 \theta d\theta \int_0^{2\pi} \sin \phi d\phi \hat{\mathbf{y}} + \int_0^\pi \sin \theta \cos \theta d\theta \int_0^{2\pi} d\phi \hat{\mathbf{z}} \right) = 0. \end{aligned}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in \mathbb{R}^3 . This implies that the first two addends within the braces in (80) vanish. Concerning now the integrals in the third and last terms on the right hand side of the same equation, we have that the integrals in \mathbf{X}^* are similar to the one in (69). Moreover, by setting $(\mathbf{a}_s \cdot \mathbf{V}^*) \mathbf{V}^* = a_s \cos \theta V^{*2} \vec{\mathbf{v}}$, with $a_s = \|\mathbf{a}_s\|$, in the integral with respect to \mathbf{V}^* appearing in the third term, and then transforming to spherical coordinates, we obtain

$$\begin{aligned} \int_{\mathbb{R}^3} a_s \cos \theta V^{*2} \vec{\mathbf{v}} \exp\left(-\frac{\mu_{is} V^{*2}}{2k_B T}\right) V^* d\mathbf{V}^* = & a_s \int_0^\infty V^{*5} \exp\left(-\frac{\mu_{is} V^{*2}}{2k_B T}\right) dV^* \left(\hat{\mathbf{x}} \int_0^\pi \sin^2 \theta \cos \theta d\theta \right. \\ & \underbrace{\int_0^{2\pi} \cos \phi d\phi}_{=0} + \hat{\mathbf{y}} \int_0^\pi \sin^2 \theta \cos \theta d\theta \underbrace{\int_0^{2\pi} \sin \phi d\phi}_{=0} + \hat{\mathbf{z}} \underbrace{\int_0^\pi \sin \theta \cos^2 \theta d\theta}_{\frac{2}{3}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \Big). \end{aligned}$$

Performing the integration with respect to V^* , we obtain

$$\int_{\mathbb{R}^3} (\mathbf{a}_s \cdot \mathbf{V}^*) \mathbf{V}^* \exp\left(-\frac{\mu_{is} V^{*2}}{2k_B T}\right) V^* d\mathbf{V}^* = \frac{4\pi}{3} \left(\frac{2k_B T}{\mu_{is}} \right)^3 \mathbf{a}_s. \quad (81)$$

Similarly, with respect to the last term on the right hand side of (80), we obtain

$$\int_{\mathbb{R}^3} (\mathbf{a}_i \cdot \mathbf{V}^*) \mathbf{V}^* \exp\left(-\frac{\mu_{is} V^{*2}}{2k_B T}\right) V^* d\mathbf{V}^* = \frac{4\pi}{3} \left(\frac{2k_B T}{\mu_{is}}\right)^3 \mathbf{a}_i. \quad (82)$$

Substituting the above results into (80) and performing a little algebra we derive the final expression (74). This ends the proof of Lemma 4.3. The computation of the $O(\alpha^2)$ terms \mathcal{P}_i and \mathcal{Q}_i is omitted here, see Appendix 6.2. \square

Remark 4.4 (a) *The diffusion coefficients in our limiting equations can be computed explicitly from expressions (74). This will be done in the next subsection, see expression (86).*

(b) *In paper [25], for another kinetic model, the authors considered a different input function (see Eq. (32) of [25]) and obtained a production term (see (34) in that paper) similar to the one in our expression (74). However, the coefficient 32/9 in our case, instead of 8/3 in paper [25], results from the fact that the models are different and also from the definition of the elastic cross sections, namely we use $\sigma_{is}^2 = (d_i + d_s)^2/4$ and paper [25] uses $\sigma_{\beta\alpha} = (d_\alpha + d_\beta)^2/16$.* \square

4.4 Macroscopic equations and formal asymptotics

In this subsection we state the main result of this paper. In particular, using Lemmas 4.1 and 4.3, we formally derive the reaction diffusion system of MS type as the hydrodynamic asymptotic limit of the scaled SRS kinetic system (53). The connection between the two systems is based on the fact that the scaled Maxwellians (55) solve the kinetic equations if the macroscopic parameters c_i^α and \mathbf{u}_i^α characterizing such Maxwellians solve the approximate equations (60) and (73). The conclusion is obtained in the limit as $\alpha \rightarrow 0$ by assuming that the functions c_i^α , \mathbf{u}_i^α converge pointwise to c_i , \mathbf{u}_i , for $t \geq 0$ and $\mathbf{x} \in \Omega$.

Theorem 4.5 (i) *The Maxwellians defined in (55) are solutions of the initial boundary value problem for the scaled SRS kinetic equations (53) with initial conditions (54) if, for $i = 1, 2, 3, 4$, functions c_i^α and \mathbf{u}_i^α solve the approximate system*

$$\begin{cases} \frac{\partial c_i^\alpha}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(c_i^\alpha \mathbf{u}_i^\alpha) = \mathcal{J}_i, \\ \alpha^2 \frac{\partial}{\partial t}(c_i^\alpha \mathbf{u}_i^\alpha) + \frac{k_B T}{m_i} \frac{\partial c_i^\alpha}{\partial \mathbf{x}} + \alpha^2 \frac{\partial}{\partial \mathbf{x}}(c_i^\alpha \mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha) = \mathcal{O}_i - \mathcal{P}_i + \mathcal{Q}_i, \end{cases} \quad (83)$$

where the reaction rate \mathcal{J}_i and the production terms \mathcal{O}_i , \mathcal{P}_i and \mathcal{Q}_i , defined respectively by (61), (74) and (75), are computed using the approximations (57) to the Maxwellians (55).

(ii) *Moreover, in the limit as $\alpha \rightarrow 0$, the system (83) reduces to*

$$\begin{cases} \frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{J}_i}{\partial \mathbf{x}} = \sigma_{ij}^2 \left(\frac{2\pi\mu_{ij}}{k_B T}\right)^{\frac{1}{2}} \left[\left(\frac{\mu_{ij}}{\mu_{kl}}\right)^{\frac{1}{2}} c_k c_l \exp\left(\frac{Q_R}{k_B T}\right) - c_i c_j \right] \\ \quad \times \left[\frac{2k_B T}{\mu_{ij}} \Gamma(2, z_i^*) - \left(\frac{\Xi_{ij}}{c_0}\right)^2 \Gamma(1, z_i^*) \right], \\ \frac{\partial c_i}{\partial \mathbf{x}} = \frac{32}{9} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \left(\frac{2\pi\mu_{is}}{k_B T}\right)^{\frac{1}{2}} (c_i \mathbf{J}_s - c_s \mathbf{J}_i), \end{cases} \quad (84)$$

whose unknowns are the concentrations c_i and the diffusive fluxes \mathbf{J}_i .

Proof. The statement in item (i) follows from Lemmas 4.1 and 4.3.

Concerning item (ii), we can write $c_i^\alpha \mathbf{u}_i^\alpha = \mathbf{J}_i^\alpha + c_i^\alpha \mathbf{u}^\alpha$, where \mathbf{u}^α represents the average velocity of the mixture relative to the scaled distributions f_i^α , see expression (50b). Letting $\alpha \rightarrow 0$ in (83), assuming that the limits

$$c_i = \lim_{\alpha \rightarrow 0} c_i^\alpha, \quad \mathbf{J}_i = \lim_{\alpha \rightarrow 0} \mathbf{J}_i^\alpha, \quad \mathbf{u} = \lim_{\alpha \rightarrow 0} \mathbf{u}^\alpha,$$

exist pointwise for any $t > 0$ and $\mathbf{x} \in \Omega$, and neglecting the convective term, that is $\frac{\partial}{\partial \mathbf{x}}(c_i \mathbf{u}) = \mathbf{0}$, we obtain the desired system (84). \square

Observe that summing the first and second equations of (84) over all species, we obtain that c is uniform in space and constant in time. Therefore, the second equation of system (84) can be rewritten as

$$\frac{\partial c_i}{\partial \mathbf{x}} = \frac{1}{c} \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_i \mathbf{J}_s - c_s \mathbf{J}_i}{D_{is}}, \quad (85)$$

where

$$D_{is} = \frac{9}{32} \left(\frac{k_B T}{2\pi \mu_{is}} \right)^{\frac{1}{2}} \frac{1}{c \sigma_{is}^2}, \quad i \neq s, \quad (86)$$

are the diffusion coefficients.

Consequently, for $i = 1, 2, 3, 4$, putting together the constraint law (6), the boundary conditions (9) for the diffusive fluxes \mathbf{J}_i , and (84) with the gradient term $\frac{\partial c_i}{\partial \mathbf{x}}$ expressed as given in (85), we obtain

$$\left\{ \begin{array}{l} \frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{J}_i}{\partial \mathbf{x}} = \mathcal{J}_i, \quad \mathbf{x} \in \Omega, \quad t > 0, \\ \frac{\partial c_i}{\partial \mathbf{x}} = -\frac{1}{c} \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{D_{is}}, \quad \mathbf{x} \in \Omega, \quad t > 0, \\ \sum_{i=1}^4 m_i \mathbf{J}_i = 0, \quad \mathbf{x} \in \Omega, \quad t > 0, \\ \nu \cdot \mathbf{J}_i = 0, \quad \mathbf{x} \in \partial\Omega, \quad t > 0. \end{array} \right. \quad (87)$$

System (87) constitutes a boundary value problem which we refer to as the reaction diffusion system of Maxwell-Stefan type.

Remark 4.6 *It is important to underline that expansion (57) was used in this paper for the explicit computation of the integrals appearing on the right hand side of the concentration and momentum balance equations (see equations (60) and (73), respectively).*

Furthermore, we note that a system of Maxwell-Stefan type with the same general structure of the one in (84) can be derived from the SRS kinetic model if we do not use expansion (57). \square

5 Conclusion

In this paper, we formally derive a reaction diffusion system of Maxwell-Stefan type as the hydrodynamic limit of the simple reacting spheres kinetic model for a quaternary mixture of monatomic ideal gases undergoing a reversible chemical reaction of bimolecular type. By considering a scaling in which elastic collisions play a dominant role in the evolution of the species while chemical reactions are slow, and using a first order correction to the Maxwellian distribution in the species rest frame, the diffusion coefficients and the chemical production

rates appearing in the species equations for the concentration and momentum have been explicitly computed from the collisional dynamics of the kinetic model.

An important aspect in our work is that we have used the same correction to the Maxwellian distribution for the computation of both elastic and reactive production terms, leading to a more consistent macroscopic picture (see Remark 4.6). Moreover, our correction to the Maxwellian distribution coincides with the one used by Stefan in his celebrated work from 1872 to derive the diffusion coefficients in a mixture of gases.

In the quoted literature about the hydrodynamic limits of kinetic models for reactive mixtures, the derivation of the MS equations had not yet been considered. Our work provides the first result in this direction and, in our opinion, complements the work developed in [11, 12, 13, 22] in the context of non-reactive mixtures.

Still in connection with the work developed in [11, 12, 13, 22] for non-reactive mixtures, we would like to emphasize here that when we turn off the chemical reaction in our model (i.e if the mixture is made up of four non-reactive species), our limiting system (87) reduces to the Maxwell-Stefan system for hard sphere molecules, which is similar to the one obtained in [12] for Maxwellian molecules.

The fact that in our analysis the mixture can react chemically allows to consider many interesting problems concerning the derivation of the MS equations from the kinetic model. Among the most interesting problems, we quote the following.

The first problem is the introduction of chemical potentials as the main agent in the definition of the driving forces and the study of the passage to the hydrodynamic limit by removing the isothermal assumption. This will certainly lead to a very rich setting from the physical but also from the mathematical point of view.

The second problem concerns the possibility of studying different time scales associated to the chemical reaction, in particular different chemical regimes, and obtaining the influence of chemical reaction in the limiting MS equations.

In fact, the scaling of slow chemical reaction studied here is the sole reason why the limit equations for the momentum of the species do not include any contributions coming from the reactive collision terms. This can be seen from Lemma 4.3, in particular, from the second equation in (83), where clearly the chemical contributions are present, but they are of order of α^2 , due to the scaling, and hence go to zero in the limit as $\alpha \rightarrow 0$.

Additionally, when studying different time scales associated to the chemical reaction, especially those chemical regimes in which reactive collisions are treated on a par with elastic ones, our SRS model results to be appropriate, because of the inclusion of the correction term in the elastic operator. This correction term, as mentioned before, singles out those pre-collisional states that are energetic enough to result in a chemical reaction, therefore preventing double counting of these collisions in the elastic and reactive operators. In this sense, the correction term leads to non anomalous results.

Finally, our next line of action will include an extension of the present analysis to kinetic models for reactive mixtures with polyatomic structure, in view of describing more meaningful chemical processes.

The problems just described above will be addressed in future works.

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6 Appendices

In this section, we provide some details about the computation of the integrals given in Section 4 that were not evaluated there.

6.1 Appendix A

In this appendix, we prove that \mathcal{E} and \mathcal{F} , given in (65) of Subsection 4.2 are null. We start with \mathcal{E} and write it as the sum of the next two terms

$$\begin{aligned}\mathcal{E}_1 &= \sigma_{ij}^2 \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 \mathbf{a}_k \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_k^\circ M_k^\alpha M_l^\alpha \Theta \left(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij} \right) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i, \\ \mathcal{E}_2 &= \sigma_{ij}^2 \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 \mathbf{a}_l \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_l^\circ M_k^\alpha M_l^\alpha \Theta \left(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij} \right) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i.\end{aligned}$$

From (58) we rewrite the integral appearing in \mathcal{E}_1 as

$$\begin{aligned}c_k^\alpha c_l^\alpha \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_k^\circ \exp \left[-\frac{m_k (\mathbf{v}_k^\circ)^2 + m_l (\mathbf{v}_l^\circ)^2}{2k_B T} \right] \\ \times \Theta \left(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij} \right) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i.\end{aligned}$$

Now we change variables from $\mathbf{v}_i, \mathbf{v}_j$ to $\mathbf{v}_k^\circ, \mathbf{v}_l^\circ$ and use the first expression of (26) given in Property 3.4 together with (25) to rewrite the previous term as

$$\begin{aligned}c_k^\alpha c_l^\alpha \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_k^\circ \exp \left[-\frac{m_k (\mathbf{v}_k^\circ)^2 + m_l (\mathbf{v}_l^\circ)^2}{2k_B T} \right] \\ \times \Theta \left(\langle \epsilon, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl} \right) \langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\epsilon d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ. \quad (88)\end{aligned}$$

Performing similar computations to those of (67), we conclude that the integral in (88) is equal to the difference of the next two integrals

$$\begin{aligned}\mathcal{E}_1^1 &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{v}_k^\circ \exp \left[-\frac{m_k (\mathbf{v}_k^\circ)^2 + m_l (\mathbf{v}_l^\circ)^2}{2k_B T} \right] V_* \Theta \left(V_* - \frac{\Xi_{kl}}{c_0} \right) d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ, \\ \mathcal{E}_1^2 &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{v}_k^\circ \exp \left[-\frac{m_k (\mathbf{v}_k^\circ)^2 + m_l (\mathbf{v}_l^\circ)^2}{2k_B T} \right] V_* \Theta \left(V_* - \frac{\Xi_{kl}}{c_0} \right) \left(\frac{\Xi_{kl}}{c_0 V_*} \right)^2 d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ,\end{aligned} \quad (89)$$

where $V_* = \|\mathbf{v}_k^\circ - \mathbf{v}_l^\circ\| = \|\mathbf{v}_l^\circ - \mathbf{v}_k^\circ\|$. Now, we look first at \mathcal{E}_1^1 . We transform the six fold integral in \mathbf{v}_k° and \mathbf{v}_l° to the centre of mass velocity $\mathbf{X}_* = (m_k \mathbf{v}_k^\circ + m_l \mathbf{v}_l^\circ)/M$ and relative velocity $\mathbf{V}_* = \mathbf{v}_l^\circ - \mathbf{v}_k^\circ$. Using the fact that the Jacobian of the transformation has absolute value 1, we obtain

$$\begin{aligned}\mathcal{E}_1^1 &= \int_{\mathbb{R}^3} \mathbf{X}_* \exp \left(-\frac{M X_*^2}{2k_B T} \right) d\mathbf{X}_* \int_{\mathbb{R}^3} \exp \left(-\frac{\mu_{kl} V_*^2}{2k_B T} \right) V_* \Theta \left(V_* - \frac{\Xi_{kl}}{c_0} \right) d\mathbf{V}_* \\ &\quad - \frac{m_l}{M} \int_{\mathbb{R}^3} \exp \left(-\frac{M X_*^2}{2k_B T} \right) d\mathbf{X}_* \int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(-\frac{\mu_{kl} V_*^2}{2k_B T} \right) V_* \Theta \left(V_* - \frac{\Xi_{kl}}{c_0} \right) d\mathbf{V}_*,\end{aligned}$$

where $X_* = \|\mathbf{X}_*\|$. Note that the integral with respect to \mathbf{X}_* in the first term on the right hand side of \mathcal{E}_1^1 is null and so the first term above vanishes. Moreover, the integral with respect to \mathbf{V}_* in the second term can be written in spherical coordinates and it is equal to

$$\int_{V_* \geq \frac{\Xi_{kl}}{c_0}}^\infty \int_0^\pi \int_0^{2\pi} V_*^4 \bar{\mathbf{v}} \exp \left(-\frac{\mu_{kl} V_*^2}{2k_B T} \right) \sin \theta d\phi d\theta dV_*,$$

where we used the fact that any vector can be written in terms of a unit vector, i.e. $\mathbf{V}_* = V_* \vec{\mathbf{v}}$, with $\vec{\mathbf{v}} = \hat{\mathbf{x}} \sin \theta \cos \phi + \hat{\mathbf{y}} \sin \theta \sin \phi + \hat{\mathbf{z}} \cos \theta$, and $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ the Cartesian unit vectors in \mathbb{R}^3 . By simple computations, we get that the previous integral is equal to zero. This shows that $\mathcal{E}_1^1 = 0$. Now, repeating exactly the same strategy as above in order to show that $\mathcal{E}_1^2 = 0$, it is enough to compute the next two integrals

$$\begin{aligned}\mathcal{E}_{1A}^2 &= \int_{\mathbb{R}^3} \mathbf{X}_* \exp\left(-\frac{MX_*^2}{2k_B T}\right) d\mathbf{X}_* \int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{kl} V_*^2}{2k_B T}\right) V_* \Theta\left(V_* - \frac{\Xi_{kl}}{c_0}\right) \left(\frac{\Xi_{kl}}{c_0 V_*}\right)^2 d\mathbf{V}_*, \\ \mathcal{E}_{1B}^2 &= \int_{\mathbb{R}^3} \mathbf{V}_* \exp\left(-\frac{\mu_{kl} V_*^2}{2k_B T}\right) V_* \Theta\left(V_* - \frac{\Xi_{kl}}{c_0}\right) \left(\frac{\Xi_{kl}}{c_0 V_*}\right)^2 d\mathbf{V}_* \int_{\mathbb{R}^3} \exp\left(-\frac{MX_*^2}{2k_B T}\right) d\mathbf{X}_*.\end{aligned}$$

Note that the integral with respect to \mathbf{X}_* in the expression of \mathcal{E}_{1A}^2 is null, so that $\mathcal{E}_{1A}^2 = 0$. The integral with respect to \mathbf{V}_* in the expression of \mathcal{E}_{1B}^2 can be written in spherical coordinates and by writing $\mathbf{V}_* = V_* \vec{\mathbf{v}}$ with $\vec{\mathbf{v}}$ a unit vector, we can easily show that it vanishes, so $\mathcal{E}_{1B}^2 = 0$. Thus $\mathcal{E}_1^2 = 0$. Since both \mathcal{E}_1^1 and \mathcal{E}_1^2 vanish, we have that $\mathcal{E}_1 = 0$. Similar computations show that $\mathcal{E}_2 = 0$. Putting all together we conclude that $\mathcal{E} = 0$.

Now we prove that \mathcal{F} given in (65) is equal to zero. As we have done above, we write it as the sum of the next two terms

$$\begin{aligned}\mathcal{F}_1 &= -\sigma_{ij}^2 \mathbf{a}_i \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i M_i^\alpha M_j^\alpha \Theta(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i, \\ \mathcal{F}_2 &= -\sigma_{ij}^2 \mathbf{a}_j \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_j M_i^\alpha M_j^\alpha \Theta(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i.\end{aligned}\tag{90}$$

Evaluating the integral over \mathbb{S}_+^2 in \mathcal{F}_1 and \mathcal{F}_2 using (67), we obtain

$$\begin{aligned}\mathcal{F}_1 &= -\sigma_{ij}^2 \mathbf{a}_i \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{v}_i \exp\left[-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T}\right] V \Theta\left(V - \frac{\Xi_{ij}}{c_0}\right) \left[1 - \left(\frac{\Xi_{ij}}{c_0 V}\right)^2\right] d\mathbf{v}_j d\mathbf{v}_i, \\ \mathcal{F}_2 &= -\sigma_{ij}^2 \mathbf{a}_j \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{v}_j \exp\left[-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T}\right] V \Theta\left(V - \frac{\Xi_{ij}}{c_0}\right) \left[1 - \left(\frac{\Xi_{ij}}{c_0 V}\right)^2\right] d\mathbf{v}_j d\mathbf{v}_i.\end{aligned}$$

In order to show that \mathcal{F}_1 and \mathcal{F}_2 vanish it is enough to compute the above integrals. Upon expanding, we obtain similar expressions to those given in (89), so that one can perform exactly the same computations as we did above to conclude that they both vanish. This shows that $\mathcal{F} = 0$.

6.2 Appendix B

In this appendix, we compute the integrals \mathcal{P}_i and \mathcal{Q}_i , that appear in (75). Our first goal is to show that

$$\mathcal{P}_i = \frac{8}{9} \frac{\mu_{ij}}{k_B T} \alpha^2 \sigma_{ij}^2 \sqrt{\pi} \frac{m_j}{M} c_i^\alpha c_j^\alpha (\mathbf{u}_j^\alpha - \mathbf{u}_i^\alpha) \left[\left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{3}{2}} \Gamma(3, z_i^*) - \left(\frac{\Xi_{ij}}{c_0} \right)^3 \Gamma\left(\frac{3}{2}, z_i^*\right) \right]. \tag{91}$$

Using Lemma 3.9 with $\varphi(\mathbf{v}'_i) = \mathbf{v}'_i$ and $\varphi(\mathbf{v}_i) = \mathbf{v}_i$, we obtain

$$\mathcal{P}_i = \sigma_{ij}^2 \alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{v}'_i - \mathbf{v}_i) f_i f_j \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i.$$

Using the first expression in (14) for \mathbf{v}'_i and writing the integral over \mathbb{S}_+^2 in spherical coordinates as described in Remark 3.1, where in both cases s is replaced by j , we obtain

$$\mathcal{P}_i = 2\sigma_{ij}^2 \alpha \frac{m_j}{M} \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{\frac{\pi}{2}} \int_0^{2\pi} (\mathbf{v}_j - \mathbf{v}_i) f_i^\alpha f_j^\alpha \Theta(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) V \cos^2 \theta \sin \theta d\phi d\theta d\mathbf{v}_j d\mathbf{v}_i.$$

Integrating with respect to ϕ and observing that

$$\int_0^{\arccos\left(\frac{\Xi_{ij}}{c_0 V}\right)} \cos^2 \theta \sin \theta d\theta = \frac{1}{3} \left[1 - \left(\frac{\Xi_{ij}}{c_0 V} \right)^3 \right],$$

we get

$$\mathcal{P}_i = \sigma_{ij}^2 \alpha \frac{4\pi}{3} \frac{m_j}{M} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V} f_i^\alpha f_j^\alpha \Theta \left(V - \frac{\Xi_{ij}}{c_0} \right) V \left[1 - \left(\frac{\Xi_{ij}}{c_0 V} \right)^3 \right] d\mathbf{v}_j d\mathbf{v}_i,$$

where $\mathbf{V} = \mathbf{v}_j - \mathbf{v}_i$ is the relative velocity and $V = \|\mathbf{v}_j - \mathbf{v}_i\|$. Now, we can split \mathcal{P}_i into

$$\begin{aligned} \mathcal{P}_i &= \underbrace{\sigma_{ij}^2 \alpha \frac{4\pi}{3} \frac{m_j}{M} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V} f_i^\alpha f_j^\alpha \Theta \left(V - \frac{\Xi_{ij}}{c_0} \right) V d\mathbf{v}_j d\mathbf{v}_i}_{\mathcal{P}_{i_1}} \\ &\quad - \underbrace{\sigma_{ij}^2 \alpha \frac{4\pi}{3} \frac{m_j}{M} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V} f_i^\alpha f_j^\alpha \Theta \left(V - \frac{\Xi_{ij}}{c_0} \right) V \left(\frac{\Xi_{ij}}{c_0 V} \right)^3 d\mathbf{v}_j d\mathbf{v}_i}_{\mathcal{P}_{i_2}}. \end{aligned} \quad (92)$$

Using (64), neglecting the quadratic term in the coefficient \mathbf{a} and transforming from \mathbf{v}_i and \mathbf{v}_j to the centre of mass velocity \mathbf{X} and relative velocity \mathbf{V} and also using the fact that the Jacobian of the transformation has absolute value 1, we obtain

$$\begin{aligned} \mathcal{P}_{i_1} &= \frac{4\pi}{3} \sigma_{ij}^2 \alpha \frac{m_j}{M} c_i^\alpha c_j^\alpha \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V} \exp \left(-\frac{MX^2 + \mu_{ij} V^2}{2k_B T} \right) V \Theta \left(V - \frac{\Xi_{ij}}{c_0} \right) \\ &\quad \times \left[1 + (\mathbf{a}_j + \mathbf{a}_i) \cdot \mathbf{X} + \left(\frac{\mathbf{a}_j m_i - \mathbf{a}_i m_j}{M} \right) \cdot \mathbf{V} \right] d\mathbf{X} d\mathbf{V}, \end{aligned}$$

$$\begin{aligned} \mathcal{P}_{i_2} &= \frac{4\pi}{3} \sigma_{ij}^2 \alpha \frac{m_j}{M} c_i^\alpha c_j^\alpha \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V} \exp \left(-\frac{MX^2 + \mu_{ij} V^2}{2k_B T} \right) \Theta \left(V - \frac{\Xi_{ij}}{c_0} \right) V \left(\frac{\Xi_{ij}}{c_0 V} \right)^3 \\ &\quad \times \left[1 + (\mathbf{a}_j + \mathbf{a}_i) \cdot \mathbf{X} + \left(\frac{\mathbf{a}_j m_i - \mathbf{a}_i m_j}{M} \right) \cdot \mathbf{V} \right] d\mathbf{X} d\mathbf{V}. \end{aligned}$$

We can split the integral appearing in \mathcal{P}_{i_1} as the sum of

$$\begin{aligned} \mathcal{P}_{i_1}^1 &= \int_{\mathbb{R}^3} \exp \left(-\frac{MX^2}{2k_B T} \right) d\mathbf{X} \int_{\mathbb{R}^3} \mathbf{V} \exp \left(-\frac{\mu_{ij} V^2}{2k_B T} \right) V \Theta \left(V - \frac{\Xi_{ij}}{c_0} \right) d\mathbf{V} \\ \mathcal{P}_{i_1}^2 &= (\mathbf{a}_j + \mathbf{a}_i) \cdot \int_{\mathbb{R}^3} \mathbf{X} \exp \left(-\frac{MX^2}{2k_B T} \right) d\mathbf{X} \int_{\mathbb{R}^3} \mathbf{V} \exp \left(-\frac{\mu_{ij} V^2}{2k_B T} \right) V \Theta \left(V - \frac{\Xi_{ij}}{c_0} \right) d\mathbf{V} \\ \mathcal{P}_{i_1}^3 &= \frac{m_i}{M} \int_{\mathbb{R}^3} \exp \left(-\frac{MX^2}{2k_B T} \right) d\mathbf{X} \int_{\mathbb{R}^3} (\mathbf{a}_j \cdot \mathbf{V}) \mathbf{V} \exp \left(-\frac{\mu_{ij} V^2}{2k_B T} \right) V \Theta \left(V - \frac{\Xi_{ij}}{c_0} \right) d\mathbf{V} \\ \mathcal{P}_{i_1}^4 &= -\frac{m_j}{M} \int_{\mathbb{R}^3} \exp \left(-\frac{MX^2}{2k_B T} \right) d\mathbf{X} \int_{\mathbb{R}^3} (\mathbf{a}_i \cdot \mathbf{V}) \mathbf{V} \exp \left(-\frac{\mu_{ij} V^2}{2k_B T} \right) V \Theta \left(V - \frac{\Xi_{ij}}{c_0} \right) d\mathbf{V}. \end{aligned}$$

Observe that the integrals with respect to \mathbf{V} in both $\mathcal{P}_{i_1}^1$ and $\mathcal{P}_{i_1}^2$ are equal. By using the fact that $\mathbf{V} = V \bar{\mathbf{v}}$ with $\bar{\mathbf{v}}$ a unit vector and $V = \|\mathbf{V}\|$, we note that writing them in spherical coordinates, it is easy to see that

they both vanish. Therefore, $\mathcal{P}_{i_1}^1 = \mathcal{P}_{i_1}^2 = 0$. The integral with respect to \mathbf{X} appearing in $\mathcal{P}_{i_1}^3$ and $\mathcal{P}_{i_1}^4$ has been computed in (69). By setting $(\mathbf{a}_j \cdot \mathbf{V})\mathbf{V} = a_j \cos \theta V^2 \hat{\mathbf{v}}$, the integral with respect to \mathbf{V} in $\mathcal{P}_{i_1}^3$ can be written in spherical coordinates as given below

$$\begin{aligned} & \int_{\mathbb{R}^3} a_j \cos \theta V^2 \hat{\mathbf{v}} \exp\left(-\frac{\mu_{ij} V^2}{2k_B T}\right) V \Theta\left(V - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V} \\ &= a_j \int_{V \geq \frac{\Xi_{ij}}{c_0}}^{\infty} V^5 \exp\left(-\frac{\mu_{ij} V^2}{2k_B T}\right) dV \left(\hat{\mathbf{x}} \underbrace{\int_0^{\pi} \sin^2 \theta \cos \theta d\theta}_{0} \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 \right. \\ & \quad \left. + \hat{\mathbf{y}} \int_0^{\pi} \sin^2 \theta \cos \theta d\theta \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 + \hat{\mathbf{z}} \underbrace{\int_0^{\pi} \sin \theta \cos^2 \theta d\theta}_{\frac{2}{3}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right), \end{aligned}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in \mathbb{R}^3 . Using the transformation $z = \frac{\mu_{ij}}{2k_B T} V^2$ together with (59), we obtain

$$\int_{V \geq \frac{\Xi_{ij}}{c_0}}^{\infty} V^5 \exp\left(-\frac{\mu_{ij} V^2}{2k_B T}\right) dV = \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}} \right)^3 \Gamma(3, z_i^*),$$

where z_i^* is defined as in (62). Therefore,

$$\int_{\mathbb{R}^3} (\mathbf{a}_j \cdot \mathbf{V}) \mathbf{V} \exp\left(-\frac{\mu_{ij} V^2}{2k_B T}\right) V \Theta\left(V - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V} = \frac{2\pi}{3} \left(\frac{2k_B T}{\mu_{ij}} \right)^3 \Gamma(3, z_i^*) \mathbf{a}_j. \quad (93)$$

Similarly,

$$\int_{\mathbb{R}^3} (\mathbf{a}_i \cdot \mathbf{V}) \mathbf{V} \exp\left(-\frac{\mu_{ij} V^2}{2k_B T}\right) V \Theta\left(V - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V} = \frac{2\pi}{3} \left(\frac{2k_B T}{\mu_{ij}} \right)^3 \Gamma(3, z_i^*) \mathbf{a}_i.$$

Putting together the previous computations and doing some algebra, we conclude that

$$\mathcal{P}_{i_1} = \frac{8\sqrt{\pi}}{9} \sigma_{ij}^2 \alpha^2 \frac{m_j}{M} c_i^\alpha c_j^\alpha \frac{\mu_{ij}}{k_B T} (\mathbf{u}_j^\alpha - \mathbf{u}_i^\alpha) \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{3}{2}} \Gamma(3, z_i^*). \quad (94)$$

Now we compute \mathcal{P}_{i_2} by repeating exactly the same computations as we did for \mathcal{P}_{i_1} . Splitting \mathcal{P}_{i_2} into four terms, we see that two of them vanish by the same reason as above and the remaining two are as given below

$$\begin{aligned} \mathcal{P}_{i_2}^3 &= \frac{4\pi}{3} \sigma_{ij}^2 \alpha \frac{m_j}{M} c_i^\alpha c_j^\alpha \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^{\frac{3}{2}}} \frac{m_i}{M} \left(\frac{\Xi_{ij}}{c_0} \right)^3 \\ & \quad \times \int_{\mathbb{R}^3} \exp\left(-\frac{MX^2}{2k_B T}\right) d\mathbf{X} \int_{\mathbb{R}^3} (\mathbf{a}_j \cdot \mathbf{V}) \mathbf{V} \exp\left(-\frac{\mu_{ij} V^2}{2k_B T}\right) \Theta\left(V - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}, \\ \mathcal{P}_{i_2}^4 &= -\frac{4\pi}{3} \sigma_{ij}^2 \alpha \frac{m_j}{M} c_i^\alpha c_j^\alpha \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^{\frac{3}{2}}} \frac{m_j}{M} \left(\frac{\Xi_{ij}}{c_0} \right)^3 \\ & \quad \times \int_{\mathbb{R}^3} \exp\left(-\frac{MX^2}{2k_B T}\right) d\mathbf{X} \int_{\mathbb{R}^3} (\mathbf{a}_i \cdot \mathbf{V}) \mathbf{V} \exp\left(-\frac{\mu_{ij} V^2}{2k_B T}\right) \Theta\left(V - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}. \end{aligned}$$

The integral with respect to \mathbf{X} appearing in $\mathcal{P}_{i_2}^3$ and $\mathcal{P}_{i_2}^4$ has been computed in (69) and the integrals with respect to \mathbf{V} can be computed as we did above to obtain

$$\left(\frac{\Xi_{ij}}{c_0} \right)^3 \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{3}{2}} \frac{2\pi}{3} \Gamma\left(\frac{3}{2}, z_i^*\right) \mathbf{a}_j \quad \text{and} \quad \left(\frac{\Xi_{ij}}{c_0} \right)^3 \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{3}{2}} \frac{2\pi}{3} \Gamma\left(\frac{3}{2}, z_i^*\right) \mathbf{a}_i.$$

Putting together the previous computations and doing some algebra, we conclude that

$$\mathcal{P}_{i_2} = \frac{8\sqrt{\pi}}{9} \sigma_{ij}^2 \alpha^2 \frac{m_j}{M} c_i^\alpha c_j^\alpha \frac{\mu_{ij}}{k_B T} (\mathbf{u}_j^\alpha - \mathbf{u}_i^\alpha) \left(\frac{\Xi_{ij}}{c_0} \right)^3 \Gamma \left(\frac{3}{2}, z_i^* \right). \quad (95)$$

Substituting (94), (95) into (92) and factorizing gives the desired expression (91).

The last term on the right hand side of (73), that is the integral \mathcal{Q}_i given in (75), can be written as the sum of the next three terms, where quadratic terms in the coefficients \mathbf{a} have been neglected,

$$\begin{aligned} \mathcal{R} &= \alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left(\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} - M_i^\alpha M_j^\alpha \right) \mathbf{v}_i \\ &\quad \times \Theta \left(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij} \right) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i, \\ \mathcal{S} &= \alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ + \mathbf{a}_l \cdot \mathbf{v}_l^\circ) \mathbf{v}_i \\ &\quad \times \Theta \left(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij} \right) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i, \\ \mathcal{T} &= -\alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} M_i^\alpha M_j^\alpha (\mathbf{a}_i \cdot \mathbf{v}_i + \mathbf{a}_j \cdot \mathbf{v}_j) \mathbf{v}_i \Theta \left(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij} \right) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i. \end{aligned} \quad (96)$$

First we prove that $\mathcal{R} = 0$. Observe that \mathcal{R} is similar to the integral \mathcal{D} given in (65) and, therefore, writing \mathcal{R} in terms of centre of mass velocity \mathbf{X} and relative velocity \mathbf{V} , and expanding the resulting integral, we realize that \mathcal{R} can be written as the difference of the two next terms

$$\begin{aligned} \mathcal{R}_1 &= \Delta \int_{\mathbb{R}^3} \mathbf{X} \exp \left(-\frac{MX^2}{2k_B T} \right) d\mathbf{X} \int_{\mathbb{R}^3} V \Theta \left(V - \frac{\Xi_{ij}}{c_0} \right) \left[1 - \left(\frac{\Xi_{ij}}{c_0 V} \right)^2 \right] \exp \left(-\frac{\mu_{ij} V^2}{2k_B T} \right) d\mathbf{V}, \\ \mathcal{R}_2 &= \frac{m_j}{M} \Delta \int_{\mathbb{R}^3} \exp \left(-\frac{MX^2}{2k_B T} \right) d\mathbf{X} \int_{\mathbb{R}^3} \mathbf{V} V \Theta \left(V - \frac{\Xi_{ij}}{c_0} \right) \left[1 - \left(\frac{\Xi_{ij}}{c_0 V} \right)^2 \right] \exp \left(-\frac{\mu_{ij} V^2}{2k_B T} \right) d\mathbf{V} \end{aligned}$$

where

$$\Delta = \pi \alpha \sigma_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha e^{\frac{Q_R}{k_B T}} - c_i^\alpha c_j^\alpha \right].$$

Since the integral with respect to \mathbf{X} in \mathcal{R}_1 is zero, we conclude that the contribution to \mathcal{R} comes only from \mathcal{R}_2 , which can be rewritten as

$$\begin{aligned} &\frac{m_j}{M} \Delta \int_{\mathbb{R}^3} \exp \left(-\frac{MX^2}{2k_B T} \right) d\mathbf{X} \int_{\mathbb{R}^3} \mathbf{V} \exp \left(-\frac{\mu_{ij} V^2}{2k_B T} \right) V \Theta \left(V - \frac{\Xi_{ij}}{c_0} \right) d\mathbf{V} \\ &\quad - \frac{m_j}{M} \Delta \int_{\mathbb{R}^3} \exp \left(-\frac{MX^2}{2k_B T} \right) d\mathbf{X} \int_{\mathbb{R}^3} \mathbf{V} \left(\frac{\Xi_{ij}}{c_0 V} \right)^2 \exp \left(-\frac{\mu_{ij} V^2}{2k_B T} \right) V \Theta \left(V - \frac{\Xi_{ij}}{c_0} \right) d\mathbf{V}. \end{aligned}$$

Transforming both integrals in \mathbf{V} above to spherical coordinates and using the fact that $\mathbf{V} = V \vec{\mathbf{v}}$ with $\vec{\mathbf{v}}$ a unit vector and $V = \|\mathbf{V}\|$, we get that both integrals vanish. This shows that $\mathcal{R} = 0$ as desired. Now we analyze \mathcal{S} , which can be written as the sum of the next two terms

$$\begin{aligned} \mathcal{S}_1 &= \alpha \sigma_{ij}^2 \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ) \mathbf{v}_i M_k^\alpha M_l^\alpha \Theta \left(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij} \right) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i \\ \mathcal{S}_2 &= \alpha \sigma_{ij}^2 \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{a}_l \cdot \mathbf{v}_l^\circ) \mathbf{v}_i M_k^\alpha M_l^\alpha \Theta \left(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij} \right) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i. \end{aligned}$$

Now we change variables from $\mathbf{v}_i, \mathbf{v}_j$ to $\mathbf{v}_k^\circ, \mathbf{v}_l^\circ$, by using the first expression of (26) given in Property 3.4 together with (25) to rewrite \mathcal{S}_1 and \mathcal{S}_2 as

$$\begin{aligned}\mathcal{S}_1 &= \alpha \sigma_{ij}^2 \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ) \mathbf{v}_k^\circ M_k^\alpha M_l^\alpha \Theta(\langle \epsilon, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \\ &\quad \times \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{1}{2}} \omega^+ \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{3}{2}} \frac{\langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle}{\omega^+} d\epsilon d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ, \\ \mathcal{S}_2 &= \alpha \sigma_{ij}^2 \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{a}_l \cdot \mathbf{v}_l^\circ) \mathbf{v}_l^\circ M_k^\alpha M_l^\alpha \Theta(\langle \epsilon, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \\ &\quad \times \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{1}{2}} \omega^+ \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{3}{2}} \frac{\langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle}{\omega^+} d\epsilon d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ.\end{aligned}$$

Therefore,

$$\begin{aligned}\mathcal{S}_1 &= \sigma_{ij}^2 \alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ) \mathbf{v}_k^\circ M_k^{\alpha\circ} M_l^{\alpha\circ} \Theta(\langle \epsilon, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\epsilon d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ \\ \mathcal{S}_2 &= \sigma_{ij}^2 \alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{a}_l \cdot \mathbf{v}_l^\circ) \mathbf{v}_l^\circ M_k^{\alpha\circ} M_l^{\alpha\circ} \Theta(\langle \epsilon, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\epsilon d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ.\end{aligned}\tag{97}$$

Performing similar computations to those of (67), we obtain

$$\begin{aligned}\mathcal{S}_1 &= \sigma_{ij}^2 \alpha \pi \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ) \mathbf{v}_k^\circ M_k^{\alpha\circ} M_l^{\alpha\circ} V_* \Theta\left(V_* - \frac{\Xi_{kl}}{c_0}\right) \left[1 - \left(\frac{\Xi_{kl}}{c_0 V_*}\right)^2\right] d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ, \\ \mathcal{S}_2 &= \sigma_{ij}^2 \alpha \pi \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{a}_l \cdot \mathbf{v}_l^\circ) \mathbf{v}_l^\circ M_k^{\alpha\circ} M_l^{\alpha\circ} V_* \Theta\left(V_* - \frac{\Xi_{kl}}{c_0}\right) \left[1 - \left(\frac{\Xi_{kl}}{c_0 V_*}\right)^2\right] d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ,\end{aligned}$$

where $V_* = \|\mathbf{v}_k^\circ - \mathbf{v}_l^\circ\| = \|\mathbf{v}_l^\circ - \mathbf{v}_k^\circ\|$.

Now, expanding \mathcal{S}_1 and transforming from \mathbf{v}_k° and \mathbf{v}_l° to the centre of mass velocity $\mathbf{X}_* = (m_k \mathbf{v}_k^\circ + m_l \mathbf{v}_l^\circ)/M$ and relative velocity $\mathbf{V}_* = \mathbf{v}_l^\circ - \mathbf{v}_k^\circ$, as well as using the fact that the Jacobian of the transformation has absolute value 1, we obtain that it can be written as the difference of the next two terms

$$\begin{aligned}\mathcal{S}_1^1 &= \sigma_{ij}^2 \alpha \pi c_k^\alpha c_l^\alpha \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X}_* - \frac{m_l \mathbf{V}_*}{m_k + m_l}\right) \left[\mathbf{a}_k \cdot \left(\mathbf{X}_* - \frac{m_l \mathbf{V}_*}{m_k + m_l}\right)\right] \\ &\quad \times \exp\left(-\frac{M X_*^2 + \mu_{kl} V_*^2}{2k_B T}\right) V_* \Theta\left(V_* - \frac{\Xi_{kl}}{c_0}\right) d\mathbf{X}_* d\mathbf{V}_*, \\ \mathcal{S}_1^2 &= \sigma_{ij}^2 \alpha \pi c_k^\alpha c_l^\alpha \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X}_* - \frac{m_l \mathbf{V}_*}{m_k + m_l}\right) \left[\mathbf{a}_k \cdot \left(\mathbf{X}_* - \frac{m_l \mathbf{V}_*}{m_k + m_l}\right)\right] \\ &\quad \times \exp\left(-\frac{M X_*^2 + \mu_{kl} V_*^2}{2k_B T}\right) V_* \Theta\left(V_* - \frac{\Xi_{kl}}{c_0}\right) \left(\frac{\Xi_{kl}}{c_0 V_*}\right)^2 d\mathbf{X}_* d\mathbf{V}_*,\end{aligned}$$

where we have used (58). Expanding \mathcal{S}_1^1 , we obtain

$$\mathcal{S}_1^1 = \sigma_{ij}^2 \alpha \pi c_k^\alpha c_l^\alpha \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} \int_{\mathbb{R}^3} (\mathbf{a}_k \cdot \mathbf{X}_*) \mathbf{X}_* \exp\left(-\frac{M X_*^2}{2k_B T}\right) d\mathbf{X}_*$$

$$\begin{aligned}
& \times \int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{kl}V_*^2}{2k_BT}\right) V_* \Theta\left(V_* - \frac{\Xi_{kl}}{c_0}\right) d\mathbf{V}_* \\
& - \sigma_{ij}^2 \alpha \pi c_k^\alpha c_l^\alpha \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} \frac{m_l}{m_k + m_l} \int_{\mathbb{R}^3} \mathbf{X}_* \exp\left(-\frac{MX_*^2}{2k_BT}\right) d\mathbf{X}_* \\
& \quad \times \mathbf{a}_k \cdot \int_{\mathbb{R}^3} \mathbf{V}_* \exp\left(-\frac{\mu_{kl}V_*^2}{2k_BT}\right) V_* \Theta\left(V_* - \frac{\Xi_{kl}}{c_0}\right) d\mathbf{V}_* \\
& - \sigma_{ij}^2 \alpha \pi c_k^\alpha c_l^\alpha \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} \frac{m_l}{m_k + m_l} \mathbf{a}_k \cdot \int_{\mathbb{R}^3} \mathbf{X}_* \exp\left(-\frac{MX_*^2}{2k_BT}\right) d\mathbf{X}_* \\
& \quad \times \int_{\mathbb{R}^3} \mathbf{V}_* \exp\left(-\frac{\mu_{kl}V_*^2}{2k_BT}\right) V_* \Theta\left(V_* - \frac{\Xi_{kl}}{c_0}\right) d\mathbf{V}_* \\
& + \sigma_{ij}^2 \alpha \pi c_k^\alpha c_l^\alpha \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} \frac{m_l^2}{(m_k + m_l)^2} \int_{\mathbb{R}^3} \exp\left(-\frac{MX_*^2}{2k_BT}\right) d\mathbf{X}_* \\
& \quad \times \int_{\mathbb{R}^3} (\mathbf{a}_k \cdot \mathbf{V}_*) \mathbf{V}_* \exp\left(-\frac{\mu_{kl}V_*^2}{2k_BT}\right) V_* \Theta\left(V_* - \frac{\Xi_{kl}}{c_0}\right) d\mathbf{V}_*.
\end{aligned} \tag{98}$$

Setting $(\mathbf{a}_k \cdot \mathbf{X}_*) \mathbf{X}_* = a_k \cos \theta X_*^2 \vec{\mathbf{x}}$, where $\vec{\mathbf{x}}$ is a unit vector, the first integral of the first term on the right hand side of (98) can be written in spherical coordinates as given below

$$\begin{aligned}
& \int_{\mathbb{R}^3} a_k \cos \theta X_*^2 \vec{\mathbf{x}} \exp\left(-\frac{MX_*^2}{2k_BT}\right) d\mathbf{X}_* \\
& = a_k \int_0^\infty X_*^4 \exp\left(-\frac{MX_*^2}{2k_BT}\right) dX_* \left(\hat{\mathbf{x}} \int_0^\pi \sin^2 \theta \cos \theta d\theta \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 \right. \\
& \quad \left. + \hat{\mathbf{y}} \int_0^\pi \sin^2 \theta \cos \theta d\theta \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 + \hat{\mathbf{z}} \int_0^\pi \sin \theta \cos^2 \theta d\theta \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right)
\end{aligned}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in \mathbb{R}^3 . Performing the integration with respect to X_* , we obtain

$$\int_{\mathbb{R}^3} (\mathbf{a}_k \cdot \mathbf{X}_*) \mathbf{X}_* \exp\left(-\frac{MX_*^2}{2k_BT}\right) d\mathbf{X}_* = \frac{\pi^{\frac{3}{2}}}{2} \left(\frac{2k_BT}{M}\right)^{\frac{5}{2}} \mathbf{a}_k.$$

The second integral of the first term on the right hand side of (98) is similar to the first integral on the left hand side of (70) and is equal to $2\pi \left(\frac{2k_BT}{\mu_{kl}}\right)^2 \Gamma(2, z_{i*})$, where $z_{i*} = \left(\frac{\Xi_{kl}}{c_0}\right)^2 \left\{\frac{\mu_{kl}}{2k_BT}\right\}$.

The integral in \mathbf{X}_* in the second and third terms on the right hand side of (98) vanishes. The first integral in the fourth term on the right hand side of (98) is similar to (69) and the second integral is similar to (93) and is equal to $\frac{2\pi}{3} \left(\frac{2k_BT}{\mu_{kl}}\right)^3 \Gamma(3, z_{i*}) \mathbf{a}_k$, where z_{i*} is as previously defined.

Putting together the previous computations and doing a little algebra, we obtain

$$\mathcal{S}_1^1 = \sigma_{ij}^2 \alpha^2 c_k^\alpha c_l^\alpha \frac{2}{M} \left(\frac{2\pi k_BT}{\mu_{kl}}\right)^{\frac{1}{2}} \left[m_k \Gamma(2, z_{i*}) + \frac{2}{3} m_l \Gamma(3, z_{i*}) \right] \mathbf{u}_k^\alpha.$$

Employing a similar strategy in the computation of \mathcal{S}_1^2 , we obtain that

$$\mathcal{S}_1^2 = \sigma_{ij}^2 \alpha^2 c_k^\alpha c_l^\alpha \frac{1}{M} \left(\frac{\Xi_{kl}}{c_0}\right)^2 \left(\frac{2\pi \mu_{kl}}{k_BT}\right)^{\frac{1}{2}} \left[m_k \Gamma(1, z_{i*}) + \frac{2}{3} m_l \Gamma(2, z_{i*}) \right] \mathbf{u}_k^\alpha.$$

Since \mathcal{S}_1 is the difference between \mathcal{S}_1^1 and \mathcal{S}_1^2 , we obtain

$$\begin{aligned}\mathcal{S}_1 = \sigma_{ij}^2 \alpha^2 c_k^\alpha c_l^\alpha \frac{2}{M} \left(\frac{2\pi k_B T}{\mu_{kl}} \right)^{\frac{1}{2}} \left[m_k \Gamma(2, z_{i_*}) + \frac{2}{3} m_l \Gamma(3, z_{i_*}) \right] \mathbf{u}_k^\alpha \\ - \sigma_{ij}^2 \alpha^2 c_k^\alpha c_l^\alpha \frac{1}{M} \left(\frac{\Xi_{kl}}{c_0} \right)^2 \left(\frac{2\pi \mu_{kl}}{k_B T} \right)^{\frac{1}{2}} \left[m_k \Gamma(1, z_{i_*}) + \frac{2}{3} m_l \Gamma(2, z_{i_*}) \right] \mathbf{u}_k^\alpha.\end{aligned}\quad (99)$$

Similarly,

$$\begin{aligned}\mathcal{S}_2 = 2\sigma_{ij}^2 \alpha^2 c_k^\alpha c_l^\alpha \frac{m_l}{M} \left(\frac{2\pi k_B T}{\mu_{kl}} \right)^{\frac{1}{2}} \left[\Gamma(2, z_{i_*}) - \frac{2}{3} \Gamma(3, z_{i_*}) \right] \mathbf{u}_l^\alpha \\ - \sigma_{ij}^2 \alpha^2 c_k^\alpha c_l^\alpha \frac{m_l}{M} \left(\frac{\Xi_{kl}}{c_0} \right)^2 \left(\frac{2\pi \mu_{kl}}{k_B T} \right)^{\frac{1}{2}} \left[\Gamma(1, z_{i_*}) - \frac{2}{3} \Gamma(2, z_{i_*}) \right] \mathbf{u}_l^\alpha.\end{aligned}\quad (100)$$

Since \mathcal{S} is the sum of \mathcal{S}_1 and \mathcal{S}_2 , we obtain

$$\begin{aligned}\mathcal{S} = \sigma_{ij}^2 \alpha^2 c_k^\alpha c_l^\alpha \frac{2}{M} \left(\frac{2\pi k_B T}{\mu_{kl}} \right)^{\frac{1}{2}} \left[m_k \Gamma(2, z_{i_*}) + \frac{2}{3} m_l \Gamma(3, z_{i_*}) \right] \mathbf{u}_k^\alpha \\ - \sigma_{ij}^2 \alpha^2 c_k^\alpha c_l^\alpha \frac{1}{M} \left(\frac{\Xi_{kl}}{c_0} \right)^2 \left(\frac{2\pi \mu_{kl}}{k_B T} \right)^{\frac{1}{2}} \left[m_k \Gamma(1, z_{i_*}) + \frac{2}{3} m_l \Gamma(2, z_{i_*}) \right] \mathbf{u}_k^\alpha \\ + 2\sigma_{ij}^2 \alpha^2 c_k^\alpha c_l^\alpha \frac{m_l}{M} \left(\frac{2\pi k_B T}{\mu_{kl}} \right)^{\frac{1}{2}} \left[\Gamma(2, z_{i_*}) - \frac{2}{3} \Gamma(3, z_{i_*}) \right] \mathbf{u}_l^\alpha \\ - \sigma_{ij}^2 \alpha^2 c_k^\alpha c_l^\alpha \frac{m_l}{M} \left(\frac{\Xi_{kl}}{c_0} \right)^2 \left(\frac{2\pi \mu_{kl}}{k_B T} \right)^{\frac{1}{2}} \left[\Gamma(1, z_{i_*}) - \frac{2}{3} \Gamma(2, z_{i_*}) \right] \mathbf{u}_l^\alpha.\end{aligned}\quad (101)$$

Now, we treat the last term on the right hand side of (96). Observe that it can be written as the sum of the following two terms

$$\mathcal{T}_1 = -\alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i (\mathbf{a}_i \cdot \mathbf{v}_i) M_i^\alpha M_j^\alpha \Theta(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i,$$

(102)

$$\mathcal{T}_2 = -\alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i (\mathbf{a}_j \cdot \mathbf{v}_j) M_i^\alpha M_j^\alpha \Theta(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i.$$

Equations (102) are similar to (97), so we can do exactly the same computations as we did above for \mathcal{S} , and we get at the end that

$$\begin{aligned}\mathcal{T} = -\alpha^2 \sigma_{ij}^2 c_i^\alpha c_j^\alpha \frac{2}{M} \left(\frac{2\pi k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} \left[m_i \Gamma(2, z_i^*) + \frac{2}{3} m_j \Gamma(3, z_i^*) \right] \mathbf{u}_i^\alpha \\ + \sigma_{ij}^2 \alpha^2 c_i^\alpha c_j^\alpha \frac{1}{M} \left(\frac{\Xi_{ij}}{c_0} \right)^2 \left(\frac{2\pi \mu_{ij}}{k_B T} \right)^{\frac{1}{2}} \left[m_i \Gamma(1, z_i^*) + \frac{2}{3} m_j \Gamma(2, z_i^*) \right] \mathbf{u}_i^\alpha \\ - 2\alpha^2 \sigma_{ij}^2 c_i^\alpha c_j^\alpha \frac{m_j}{M} \left(\frac{2\pi k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} \left[\Gamma(2, z_i^*) - \frac{2}{3} \Gamma(3, z_i^*) \right] \mathbf{u}_j^\alpha \\ + \sigma_{ij}^2 \alpha^2 c_i^\alpha c_j^\alpha \frac{m_j}{M} \left(\frac{\Xi_{ij}}{c_0} \right)^2 \left(\frac{2\pi \mu_{ij}}{k_B T} \right)^{\frac{1}{2}} \left[\Gamma(1, z_i^*) - \frac{2}{3} \Gamma(2, z_i^*) \right] \mathbf{u}_j^\alpha\end{aligned}\quad (103)$$

Finally, since $\mathcal{R} = 0$, we obtain

$$\mathcal{Q}_i = \mathcal{S} + \mathcal{T}, \quad (104)$$

with \mathcal{S} and \mathcal{T} given by (101) and (103), respectively.